TECHNICAL REPORT
72-33-FL

RECOVERY OF COMPRESSED DEHYDRATED FOODS
PHASE II

by
A. P. MacKenzie
and
B. J. Luyet

American Foundation for
Biological Research

RFD 5, Box 137,
Madison, Wisconsin 53704

Contract No. DAAG17-67-C-0126
December 1971

UNITED STATES ARMY
NATICK LABORATORIES
Natick, Massachusetts 01760

Food Laboratory
FL-148

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FOREWORD

This investigation represents a continuation of the effort reported in U. S. Army Natick Laboratories Technical Report 70-16-FL, dated July 1969. As noted previously, this study has been conducted in conjunction with a program directed to achieving a significant reduction in the volume of dehydrated food components required for operational rations and packets. Prior experiments have shown that most freeze-dried foods, properly plasticized, can be compressed to volumes ranging from one-third to one-twentieth of their initial volumes and that, on rehydration, they recover spontaneously their prefrozen appearance and texture without consequential fragmentation or other damage resulting from compression. This investigation seeks to extend knowledge of controllable factors which favor the reversible compression of various food types. In addition, consideration is given to identifying changes incident to compression and to structural components contributing to reversibility.

This investigation was performed at the American Foundation for Biological Research, R.5, Madison, Wisconsin 53704 under contract DAAG17-67-C-0126 of Food Processing and Preservation Techniques, Project 1M624101D553. Dr. Alan P. MacKenzie served as Principal Investigator in association with Dr. B. J. Luyet, Director of the American Foundation for Biological Research. They were assisted by T. A. Kuster, A. R. Kutchera, J. E. Mundstock, G. R. Orndorff, L. L. Rapatz and D. H. Rasmussen of the referenced Institute. Drs. Maxwell C. Brockmann and Karl R. Johnson served as Project Officer and Alternate Project Officer, respectively, for the U. S. Army Natick Laboratories.

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ABSTRACT

Twelve foods, alone and in combination, were frozen at various rates, freeze-dried in different ways and brought to certain predetermined water contents by exposure, via the vapor phase, to water at controlled activities (a_w's). The moist freeze-dried materials were subjected to compression and to further drying, after which they were rehydrated.

It was found that processing conditions insuring best recoveries could be defined in terms of water activities to which foods were adjusted prior to compression; that is, the conclusion drawn on the basis of the Phase I studies was confirmed and extended. It was, moreover, shown that composite foods were more likely to respond well to compression where component items were selected on the basis of compatible a_w-dependent behavior.

The times taken by foods freeze-dried by conventional methods to reach constant water contents by contact with atmospheres of intermediate a_w were found not to exceed several hours. Moistening via the vapor phase proved to possess special advantages where foods destined for compression were freeze-dried in admixture.

Freeze-drying by sublimation and direct desorption of remaining water to various predetermined water activities was subjected to further analysis. Pilot-scale apparatus was designed, constructed, tested, and operated successfully.

Supplementary studies were completed in continued attempts to define factors responsible for recovery. Whole and solvent-extracted foods were examined by light and scanning electron microscopic techniques. Indications of the nature of certain irreversible changes resulting from compression were obtained.

INTRODUCTION

This report describes the second part of a study undertaken:

(1) to develop procedures assuring full recovery of representative dehydrated foods, after compression,

(2) to describe the mechanisms operating during this recovery,

(3) to characterize irreversible changes precluding full recovery.

The work to be described was, in most respects, conducted to permit a continued comparison of different methods of preparing freeze-dried foods for compression. Special attention was, once again, devoted to the examination of the relative merits of methods based on (i) resorption from a too-dry, freeze-dried state, (ii) direct desorption by "limited freeze-drying" (see the previous Final Technical Report).

As before, the major effort was directed to the systematic observation of the restoration of foods with reference to water activity (a_w), prior to compression, and to the measurement of the dependence of water content on a_w. The findings will, we hope, be seen as further proof of the potential worth of procedures based on the concept of water activity.

Supplementary studies were conducted, much as they were during Phase I, to furnish evidence of the cytological and/or the physicochemical basis of the behavior during compression in selected cases. Hopefully, the value of the several methods employed has been demonstrated.

MATERIALS

Apples (Cortland, McIntosh, Red Delicious, Winesap, and Yellow Delicious), beef (sirloin tip, graded U. S. Choice, selected for leanness), carrots (fresh, 1 to 1 1/2 inches in diameter), chicken (ready-to-cook whole breasts, about 8-oz. each), cottage cheese (creamed and dry, large curd), gravy mixes (various, dehydrated), mushrooms (fresh about 1 1/2 inches diameter, noodles (flat, 5.5% egg solids), pineapple (canned, unsweetened pack and fresh), potatoes (sliced dried and whole fresh), tuna (fancy, solid pack Albacore, in water), white sauce mixes (various), and additional ingredients for gravies and sauces were purchased at local supermarkets.

Red-Core Chantenay carrots and Early Frosty peas obtained and frozen but not used in the course of Phase I activities were removed from frozen storage at -40°C.

METHODS

1. Preparation for Freezing.

(a) Apples were peeled, cored, and cut into rings 1/4 inch thick. The rings were dipped in a 1% ascorbic acid solution, covered, and drained.

(b) Beef stew: preliminary studies. To obtain potatoes capable of adequate recovery subsequent to compression at a water activity best for beef, carrots and peas, we (i) attempted to impregnate freshly sliced potatoes with glycerol, (ii) cooked dried potato slices in aqueous glycerol and sorbitol solutions. To determine the most suitable gravy formula, different beef extracts, beef soups, prepared gravies, milk solids, starches, salts and seasonings were mixed in various proportions. Numerous preliminary experiments involving freezing, freeze-drying, humidification, compression, and rehydration were completed in each instance to determine best preparative procedures (see Discussion). Best ways to prepare potato

and gravy consistent with the requirements were decided on the basis of numerous preliminary observations on the effects of freezing, freeze-drying, humidification, compression, and rehydration on these components (see Discussion). Best quantities of each ingredient were also determined experimentally.

(c) Beef stew: final procedure. Beef, carrots and peas were precooked separately in boiling water for 15, 10 and 5 minutes respectively. Potatoes were boiled in a 15% sorbitol solution for 10 minutes. The ingredients were quickly drained and mixed into the hot gravy according to the following recipe.

Ingredients	Weights
Beef, sirloin tip, lean, 1 cm. cubes	500 g.
Carrots, 1 cm. cubes	300 g.
Peas	300 g.
Potatoes, dried, sliced	175 g.
Gravy (beef boullion, canned, double strength, 640 g.; water 220 g.; starch, phosphorylated, 48 g.; boullion cubes (3), 12 g.)	920 g.

(d) Chicken breasts were deboned and cut into three or four strips each (being cut as much as possible parallel and perpendicular to the muscle fibers). Each piece, tightly wrapped in aluminum foil, was immersed in boiling water for 30 minutes, removed, chilled to 2°C., and cut into pieces approximately 1 cm. cubed.

(e) Cottage Cheese did not require additional preparation.

(f) Pineapples were trimmed and cut into slices 1 cm. thick; woody tissues were cut away. Canned unsweetened pineapple slices (also 1 cm. thick) were drained free from fluids, under cover, on several thicknesses of filter paper.

(g) Tuna noodle casserole: preliminary studies. To obtain a mixture exhibiting uniformly good restoration following compression at a single water activity it appeared to be necessary (i) to incorporate a certain quantity of glycerol into the noodles, (ii) to pay special attention to

the formulation of a suitable white sauce. The best methods for preparing noodles and white sauce consistent with other requirements were determined on the basis of a number of preliminary experiments (see Discussion). Several additional tests were made to determine the best ratios of the components of the casserole.

(h) Tuna noodle casserole, final procedure. Noodles were rehydrated and cooked for 10 minutes in a boiling 10% aqueous glycerol solution, drained and mixed with freshly heated white sauce. To this mixture were added cold fresh mushrooms and tuna meat, cut and broken respectively, into pieces from one to three cm. across. The mixture was made according to the following recipe.

Ingredients	Weights
Mushrooms, sliced	60 g.
Noodles, glycerolated	120 g.
Tuna, water-pack	200 g.
White Sauce (non-fat dry milk solids, 38 g.; corn starch, 6 g.; seasoning salt, 18 g.; water, 258 g.)	320 g.

2. Freezing

The various foods (single components and mixtures of same) were frozen at one or more of five different rates in accordance with requirements of particular experiments. The greatest care was taken always to prevent foods from undergoing any surface drying prior to freezing.

Slow Freezing. Each food was spread one layer thick (apple slices, beef cubes, chicken cubes, mushrooms, pineapple, potato slices, and tuna flakes) or in multi-layers one to 2 cm. thick (beef stew, cottage cheese, gravy, noodles, tuna casserole, and white sauce) on Teflon-coated aluminum trays and placed on wooden tables in a cold room maintained at -30° or at -40° ± 1°C. In certain cases foods were, in addition, frozen very slowly by similar exposure to still air in a room maintained at -10° ± 1°C.

Rapid Freezing. Beef, carrots, chicken, cottage cheese, noodles, pineapple, and tuna, were frozen by the rapid method found during the First Phase to be the most convenient. Powdered carbon dioxide and food were simultaneously added into an insulated container at rates arranged to provide approximately two pounds of solid carbon dioxide per pound of food stuff. That is, the pieces of food were separated each from the other by the freezing medium. Food and refrigerant were each recovered after about 30 minutes with the aid of sieves.

Beef, carrots and chicken were also frozen very rapidly by immersion, piece by piece, in liquid nitrogen.

3. Frozen Storage.

All the foods were placed after freezing in polyethylene bags, five to ten pounds to a bag, and stored in large protective containers in a cold room at -40±2°C.

4. Freeze-Drying and Associated Operations.

Two fundamentally different freeze-drying techniques were employed to convert foods to states suitable for compression. In some experiments the frozen materials were freeze-dried "at room temperature" according to a conventional procedure to moisture contents in the range 1 to 2% per 100 g. dry product. These freeze-dried products were then moistened prior to compression by exposure, via the vapor phase, at 25°C., to sources of water of predetermined water activity (a_w)*. In other experiments frozen foods were subjected to "limited freeze-drying" during which the water activity was reduced to various predetermined values in the course of a single operation.

*We have discontinued the use of the term "relative humidity," employed throughout the previous report, in favor of the expression "water activity."

The methods are outlined in the following subsections. Since, however, the procedures employed were in many cases identical to those used and reported previously*, certain details have been omitted.

(a) Freeze-drying "at room temperature"

(i) Production experiments. Materials destined for compression/restoration experiments, cytological studies, scanning electron microscopy, and sensory evaluation were prepared in one of several apparatus of the form outlined in Fig. 1. Foods frozen by methods described in previous sections were placed in precooled sample chambers. The latter were then quickly attached to an apparatus, evacuated, and allowed to warm, as drying progressed, to the temperature of the surroundings (20 to 25°C.). The highest possible vacuum was maintained throughout the course of each run. No attempts were made to slow or to speed the warming of the sample chamber (or of the contents) to 25°C. Thus, essentially, the materials were subjected to a mild form of commercial processing. Further procedural details are to be found in the report on Phase I activities (pp. 5, 6, 11, 12).

(ii) Rate Measurements. Indications of rates of freeze-drying at room temperature were obtained in the same freeze-drying equipment employed in the previous study. The apparatus (shown in Fig. 2) incorporated a continuously recording, "null-type" Cahn R.H. Electro-balance with which sample weight was followed throughout freeze-drying. Heat transfer to the sample (20 g., more or less, contained in a wire mesh basket suspended in the sample chamber) was accomplished partly by radiation, partly by conduction through the vapor. Efforts were made to duplicate the conditions obtained in the production of larger quantities in the other apparatus.

(b) Limited Freeze-Drying

The term "Limited Freeze-Drying" was applied by Dr. A. P. MacKenzie to a process by which foods, microorganisms,

* The reader is referred to the Final Technical Report on Phase I activities for additional descriptions.

and various model systems were subjected with considerable success to differing degrees of partial dehydration at different subfreezing temperatures (see the previous Final Technical Report).

The principle of the method is evident from the block diagram reproduced in Fig. 3. When sample chamber and condenser temperatures are separately controlled, each within narrow limits (± 0.1 deg. C. each), freeze-drying proceeds by simultaneous sublimation of ice and limited desorption of unfrozen water. While the sublimation proceeds to completion, the desorption process stops when the vapor pressure of the water in the product is reduced to that of water vapor in the sample chamber in equilibrium with ice on the condenser. Greater sample chamber/condenser temperature differences result in smaller ultimate a_w's in the sample chamber; hence greater desorption from the samples. Generally, the selection of sample chamber temperatures in the range -10 to -40 and sample chamber/condenser temperature differences in the range 2 to 20 degrees C. permits the production of materials containing 25 to 5 g. H_2O per 100 g. dry solids (more or less).

(i) Production experiments. Approximately 100-g. quantities of each of 10 foods were prepared for compression/restoration studies in an apparatus of the type depicted in Fig. 4. In each instance, foodstuffs were exposed in the sample chamber to surroundings maintained at -10 ± 0.1°C. and to water-vapor-pressures tending, during freeze-drying, to that of ice on a condenser maintained at -12.9 ± 0.1°C. That is, limited freeze-drying was conducted first in each case to completion at a water activity of 0.7 (± 0.01)*.

Quantities of materials were then removed to storage. When the apparatus was reevacuated, the condenser temperature was lowered (to -14.6 ± 0.1°C.) to yield an a_w, at -10°C., of 0.6. When the ensuing further desorption was completed additional samples were removed from the apparatus. Materials subjected to limited freeze-drying at -10°C. and to further desorption were, in the same way, removed from the apparatus after successive stepwise equilibration to water activities of 0.5, 0.4, 0.3, 0.2, and 0.1.

(ii) Determination of extent of water retention — desorption isotherms at -10°C. The necessary desorption experiments

*We have followed the practice of defining a_w below 0°C. with reference to vapor pressures of liquid water cited by Mason (1957). Working tables based on Mason's values are, along with the latter, reproduced in an appendix to this text.

were made either in an apparatus of the type described in the previous section (in which materials were also prepared in greater quantities) or in an apparatus for limited freeze-drying incorporating a continuously recording balance (essentially the apparatus illustrated in Fig. 2, modified in accordance with the requirements outlined in Fig.3).

In the first instance the apparatus was opened daily. The samples were weighed always in a room at -10°C., and returned to the apparatus. In the latter case the weight of the sample was obtained in the form of a continuous recording.

Each product was, in any case, reduced by limited freeze-drying to a constant weight at -10°C. appropriate to an a_w equal to 0.70. Further successive reductions to constant weight were obtained in each case by exposure, in sequence, to water activities of 0.6, 0.5, 0.4, 0.3, 0.2, 0.1, 0.05, 0.025, all at -10°C. Water contents based on the sample weight at 0.00 a_w (obtained at 20°C. rather than at -10°C.) were plotted as functions of a_w (and thus of relative humidity) to yield desorption isotherms.

In one case a special series of determinations was made in which a_w and temperature were each altered in a cyclic, progressive manner. This series was accomplished in the apparatus incorporating the recording balance as follows. Limited freeze-drying was completed at -10°C. to a 0.50 a_w at which stage the large valve between the balance/sample chamber assembly and the condenser was closed. Effectively isolated at constant water content, the sample was allowed to warm to room temperature. The water vapor pressure corresponding to the equilibrium established at room temperature was noted, the sample was cooled to -10°C., and the equilibrium pressure noted once again. The valve to the condenser was then opened, insuring the return of the sample to 0.50 a_w. Changes in sample weight arising in the course of the 4-step cycle were noted. Desorption was then extended, at -10°C., to a 0.30 a_w at which stage the sample was exposed to the same isolation/warming/cooling/reconnection procedure.

Desorption was subsequently extended at -10°C. to water activities of 0.30, 0.09, 0.05, at each of which the sample was exposed to the isolation/warming/cooling/reconnection procedure. Changes in water vapor pressure and sample weight were in each case noted.

(iii) Pilot-scale studies. See separate description (Section 5).

(c) Humidification.

Foods freeze-dried in the usual way to low water contents were moistened prior to compression by exposure to water vapor as follows:

(i) Resorption isotherms. Quantities of each of 12 test materials freeze-dried at room temperature were taken from storage over dry Linde Molecular Sieve, weighed and distributed between 8 vacuum desiccators, each partly filled with aqueous sulphuric acid. The weights of the 12 materials thus exposed, in vacuo, to solutions having water activities of 0.10, 0.20, 0.30, 0.40, 0.50, 0.60, 0.70, and 0.80 were determined periodically, also the times beyond which these weights did not change further. Later the samples were exposed a second time to dry Linde Molecular Sieve to permit the redetermination of the dry weight. Water resorbed per unit weight of dry product at 25°C. was plotted as a function of water activity in each case.

(ii) Preparation for compressibility studies and for sensory evaluation. Larger quantities of each material were similarly prepared for studies on the effects of different degrees of resorption on compression and on subsequent recovery. Resorption was allowed to proceed for times equal to those taken by samples to reach constant weight in previous tests. Quantities of certain foods destined for taste panel studies were prepared in numbers of large desiccators in much the same way with the following differences:

(1) Sulphuric acid solutions generating precisely the required water activities were poured into the desiccators, (2) weights of water equal to those to be taken up by the foods (the values were obtained from the dry weights of the foods and the resorption isotherms) were added slowly to the sulphuric acid solutions, (3) the sulphuric acid was stirred slowly and continuously by means of magnets after the foods were sealed in the desiccators.

(iii) Rate measurements. As in the earlier studies we used the freeze-drying apparatus incorporating the continuously recording balance to measure humidification

velocities. Atmospheres of required water activity were obtained by suitable choice of condenser temperature. Resorption was initiated when the valve between the sample chamber containing the fully dried specimen and the condenser (now acting as source of water) was opened. Further procedural details may be found in the report on Phase I studies.

(d) Compression

(i) Physical compression/restoration studies. Moistened freeze-dried foods were compressed in small quantities (several g. on a dry weight basis) between aluminum plates mounted in a hydraulic press. Pressures employed were calculated on the basis of observed pressure readings and measurements of product area after compression. Pressures were maintained at certain constant values for periods, generally, of one minute.

(ii) Sensory evaluation. Compression of larger quantities was accomplished 250 ml. at a time in an aluminum cylinder having smooth-faced aluminum discs, closely fitting the cylinder walls, for sliding ends (Fig. 5). The cylinder was filled with the freeze-dried food having the desired moisture content, closed and inserted in the press. Each material was subjected to 500 p.s.i. of sample area for one minute, after which the pressure was quickly released.

(e) Final drying and storage.

(i) Drying and storage. Compressed materials were dried in vacuum desiccators, over dry Linde Molecular Sieve, at 25°C. Bulk densities before and after final drying were determined from measurements of sample area, thickness and weight. Final storage was effected in vacuum, over dry Linde Molecular Sieve, at 2°C.

(ii) Rate measurements. Final drying rates were determined immediately resorption was completed (see the previous page). Resorbed specimens were removed from the apparatus containing the recording balance, subjected to 500 p.s.i. for one minute, and returned to the suspended basket. The condenser temperature was lowered to -196°C., the sample being kept the meanwhile at 25°C. Wide-bore valves were open through-

out the system during final drying, thus insuring the completion of the process under high vacuum.

(f) Recovery

(i) Observations. Pieces of various foods at different water contents were subjected to various pressures for different periods of time, to final drying in some cases, and to rehydration in water. Each sample's behavior was noted with reference to orientation, pressure, duration of compression, and to the method used to permit restoration (flotation vs. forced immersion; hot water vs. cold water). Foods were examined one at a time and, afterwards, in appropriate admixture.

In certain instances foods subjected to closely defined rehydration for specified periods were transferred to fixative solutions preparatory to cytological studies — see later.

(ii) Taste panel studies. Various standardized procedures determined on the basis of preliminary studies were applied to the rehydration of larger quantities for sensory evaluation. (See Results.)

5. Design and Construction of Pilot-Scale Equipment.

To study the ways in which the limited freeze-drying process might be scaled up to permit the production of large quantities of food suitable for compression, an analysis of the heat and mass transfer problems involved was completed. On the basis of the concepts embodied in previous all-glass laboratory systems and from the above-mentioned engineering analysis an all-metal pilot-scale apparatus was designed and built. Provision was made for the handling of 5 to 10-pound quantities of frozen foods at a time. Special efforts were made to produce an apparatus easy to load, unload and clean.

The set-up, illustrated in Fig. 6, was designed to operate in a cold room in which there were no appreciable variations in temperature. That part of the set-up designed

to operate in a room maintained at -10°C. (or, in other circumstances, at -20, for example) is shown in Fig. 7. Not shown are the multipoint temperature recorder and the pneumatic regulator controlling the sample chamber/condenser temperature difference; these latter units were located in a nearby room kept at 25°C.

The sample chamber components and condenser were supported on and within, respectively, a welded steel framework in such a way that vapor flowed downwards from sample to condenser. The sample chamber was designed to maintain sample supports at the temperature of the surrounding air, that is, to restrict temperature gradients, effectively, to the material undergoing freeze-drying. The chamber was assembled from circular plates and rings of aluminum. When, during the loading operation, a sufficient number of layers of frozen food was obtained, the uppermost module was capped with one last plate to which was attached an adapter connecting to two vacuum gauges and an inlet valve.

The condenser was formed from a stainless steel vessel jacketed with cooled ethanol contained in a second, insulated stainless steel container. Continuous stirring ensured the absence of temperature gradients within the ethanol. The connection between sample chamber and condenser was made by wide tubing incorporating a stainless steel butterfly valve closure of which permitted tests for the completion of sublimation by "vapor pressure rise to equilibrium." Further connections between condenser and vacuum pump were by narrower tubing incorporating the same type of throttling devices employed in previous all-glass apparatus for limited freeze-drying. Additional vacuum gauges were located as shown, the better to permit quick checks on the performance of the equipment.

Constant sample chamber temperature was obtained through the close control of the temperature of the surrounding air (-10 ± 0.25°C.). Constant sample chamber/condenser temperature difference was achieved with a part electrical, part pneumatic system. A Honeywell Air-O-Line unit proportioned the passage of precooled air through coils immersed in the bath surrounding the condenser. The unit functioned in response to the signal from a thermocouple one junction of which was attached to the sample chamber surface. The other junction was immersed in the coolant surrounding the condenser.

The mechanical pump, the vacuum gauges, and the stirrer were operated without difficulty at -10°C. Such heat as these units released was absorbed by the air in the room, the temperature of which was readily maintained at -10°C. In other respects the equipment was operated according to procedures developed on all-glass apparatus for limited freeze-drying.

6. Observations in the Freeze-Drying Microscope.

The dependence on freeze-drying temperature of the nature of the visible changes occurring during freeze-drying was followed in certain instances in a specially equipped microscope. Fluid food components — extracts, gravies, and sauces — were examined in layers 10 to 20 μm. thick, formed and frozen between two glass plates. The apparatus, properly assembled, allowed an operator to observe and record the characteristic appearance of the frozen portion, the "freeze-drying front," and the freeze-dried matrix (all in a plane perpendicular to the direction of the viewing axis). The temperature of the freeze-drying front, or "subliming interface," was adjusted to various desired values, generally in the range -10 to -50°C., and maintained in each instance within 0.1°C. of the chosen value. Additional operating details may be found in the original description of the apparatus (MacKenzie, 1964).

7. Cytological Studies.

To determine the combined effect of the compression and restoration procedures on the microscopic structure, certain foods were subjected to conventional cytological study. Foods were cooked (where necessary), frozen, freeze-dried, humidified to various predetermined extents, compressed, subjected to final drying and, lastly, to rehydration (in hot or cold water, whichever resulted in better recovery). The rehydrated materials were fixed in formalin-acetic acid-ethyl alcohol (F.A.A.), dehydrated in graded mixtures of water, ethanol, and n-butanol, and infiltrated with paraffin, m.p. 56 to 58°C., at 60°C.

Ten, 15 and 20 μm. sections were cut in longitudinal and transverse directions with steel blades on a rotary microtome at 25°C. Ribbons consisting of serial sections were attached to glass slides, stained, examined and photographed, principally at a magnification of 100×. Generally we followed the procedures described by Jensen (1962) and Sass (1964).

Control experiments were conducted in each case on fresh and/or cooked materials, and on fresh and/or cooked materials subjected also to freezing, freeze-drying and rehydration.

8. Studies on the Effects of Solvent Extraction.

Experiments were undertaken much as they were during the first phase of this study to determine the behavior of the various insoluble structural components of different foods, during compression, in conditions in which certain components were absent. Solvent extraction was used to effect the removal of lipids, after freeze-drying, from cooked beef and cooked chicken. Sugars and other water soluble substances were extracted from freeze-dried fresh apple and freeze-dried canned pineapple. The methods were as follows.

(a) Cooked beef and chicken were cut into 1 cm. cubes, subjected to slow freezing (in air at -40°C.), freeze-drying at room temperature and to 48-hr. Soxhlet extraction with chloroform/methanol mixtures (2:1, v/v).

Solvent extracted materials were stored in vacuo in desiccators containing Type 13× Linde Molecular Sieve in which conditions any solvent molecules remaining in the food were transferred to the Sieve.

(b) Apple and pineapple were frozen in air at -40 in the form of thin (0.5 to 1.0 cm.) slices, freeze-dried at room temperature and subjected to repeated extraction with stirred aqueous ethanol (40:60, v/v) at 15°C. The water alcohol mixture was changed four times at daily intervals and replaced, after the last change, with distilled water. After a further interval, the tissues were removed, drained, frozen in liquid nitrogen, and freeze-dried a second time.

The beef, chicken, apple and pineapple were then placed in desiccators containing aqueous sulphuric acid solutions adjusted to yield, upon equilibration, a_w's of 0.20, 0.30, 0.40, 0.50, 0.60, 0.70, and 0.80 at 25°C. When the desiccators were opened the samples were subjected to pressures of about 500 p.s.i. for periods of 1 minute and examined for tendencies to recover original shapes, sizes and textures in water.

9. Scanning Electron Microscopic Studies.

The suitability of the scanning electron microscope to compression studies was described and discussed in the previous Final Technical Report. We continued to use the scanning type instrument (1) to gain further information not readily obtained from thin sectioning studies, (2) to test certain additional new ways of preparing the specimens. Raw beef was selected for detailed examination.

To create sample surfaces from which the presence of typical 3-dimensional structures might be deduced, special sectioning techniques were developed, as follows:

A portion of a batch of slowly frozen beef freeze-dried at room temperature was submitted to solvent extraction with chloroform/methanol (see the previous section). Whole and solvent-extracted freeze-dried materials were then moistened by exposure to water vapor in desiccators set up to maintain a_w's of 0.20, 0.50, and 0.80 at 25°C. Equilibrated materials were subjected to 500 p.s.i. for one minute and dried over Molecular Sieve.

Dried, compressed materials were infiltrated with paraffin wax (melting point 56 to 58°C.) and sectioned at 25°C. Sections were cut and discarded until structures of a desired, uniform orientation were seen in the face of the block exposed to the knife. Blocks were then submitted 1) to several successive solvent extractions from xylene, 2) to vacuum to remove last traces of the latter solvent. Great care was taken to protect the cut surfaces from contact with glassware and other solid objects.

Control specimens were prepared by frozen sectioning and freeze-drying. Suitable surfaces were obtained by sectioning frozen beef on a specially modified microtome,

portions of which were operated under liquid nitrogen. Frozen specimens shaved on one face at -196°C. were freeze-dried at -40°C. in a high vacuum.

All the specimens were transferred to a dry-box (2 to 5% R.H.), inspected under low power microscopes, mounted cut surfaces uppermost, and attached to metal stubs with cellulose nitrate cement. The specimens were then coated in vacuo with gold-palladium alloy. To provide the continuous metallic coatings necessary to render the sample surfaces electrically conducting under the scanning electron beam, all the samples were rotated continuously during deposition of the heavy metal alloy. After the coating operation, specimens were stored and, when necessary, transported in glass vacuum desiccators charged with Molecular Sieve.

RESULTS

This presentation of the results of the Phase II Study follows, in most ways, the form adopted in the Final Technical Report on Phase I activities. The results are presented under ten headings, the first of which covers studies designed to complete the final choice of ingredients and preparative procedures. The second and third headings relate to compression/restoration behavior, the fourth to water content prior to compression. The fifth and sixth subsections report work relating to quantity production; the last four report relevant basic studies.

Freezing, frozen storage, and freeze-drying at room temperature were accomplished in every case without difficulty. Separate subsections describing the results of these operations have therefore been omitted.

1. Preliminary research.

Small scale studies were conducted to determine best variety, best gravy, best sauce, and best recipe, where necessary. Best choice was judged on the basis of response to freezing, freeze-drying, moistening, compression, drying,

and reconstitution. Physical compression/recovery tests and informal 4-man taste panel studies determined:

(a) That Winesap apples offered performance superior to that of Cortland, Delicious (Red or Yellow), or McIntosh;

(b) That creamed cottage cheese was preferable to the dry curd product; large curd better than small curd;

(c) That the best gravy contained the least sodium chloride and the most protein and soluble starch consistent with flavor requirements and absence of a whitening effect;

(d) That the most suitable potato was obtained by the rehydration of dried potato slices in aqueous sorbitol solution, prior to freezing;

(e) That the best white sauce included the least possible sodium chloride, the least possible corn starch and the most nonfat dry milk solids consistent with the required stiffness and opacity;

(f) That the most acceptable noodles resulted from the exposure, prior to freezing, of egg noodles to aqueous glycerol;

(g) That the best beef stew and tuna noodle casserole were obtained from combinations of ingredients in proportions outlined earlier in this report.

Special efforts were made to formulate gravies and white sauces having high "collapse temperatures," these temperatures being determined according to criteria developed by MacKenzie (1965,1967). Numerous preparations were, that is, examined in the freeze-drying microscope to determine whether or not there existed in every case a freeze-drying temperature below which freeze-drying progressed with complete retention of the solute distribution characteristic of the frozen state. We observed in each case that the gravies and sauces underwent freeze-drying by one of two mechanisms depending on the temperature; that is, the dehydration progressed with the retention of the solute matrix structure below a certain freeze-drying temperature and with collapse above it. We could not obtain a gravy satisfactory from other points of view with a collapse temperature higher than -32°C.; nor was it possible, on a similar basis, to formulate a white sauce that retained its matrix when freeze-dried above -27°C.

It was, however, observed that different gravies, freeze-dried below their respective collapse temperatures of -32, or thereabouts, responded differently to exposure to 25°C. and water activities in the range 0.4 and 0.8. High salt or high sodium glutamate mixtures collapsed on moistening to 0.5 a_w or more; starch/boullion gravies collapsed at 0.6 a_w and higher, and starch/nonfat dry milk solids/beef broth mixtures survived exposures to 0.7 a_w without collapse.

2. Compression/Restoration Experiments. Behavior With Respect to Water Activity.

The results of the laboratory tests combining physical and subjective evaluation by two assistants are presented in Tables I and II. Behavior is listed according to food, method of preparation, water activity and, in some cases, freezing rate. A_w's were measured at the temperatures at which the respective sorption equilibria were established (25°C. for resorption, -10°C. for desorption). Table I describes the reactions of foods frozen slowly prior to freeze-drying at room temperature, Table II the behavior of foods prepared by slow and rapid freezing and by limited freeze-drying.

Good restoration was observed in cooked white chicken muscle after slow freezing but not after rapid freezing. When good recovery was observed it was found in each case at only one water activity; i.e. recovery was strongly a_w-dependent.

An acceptable restoration was likewise obtained with specially processed sliced potatoes (see Methods) at one a_w. Performance was, however, very strongly dependent on a_w (Table I only). Several varieties of fresh mature potatoes lost much of their respective textures after freeze-drying and rehydration and further proved to be quite unsuitable for compression.

Beef stew, judged as a composite dish, recovered an adequate overall quality somewhat less dependent on a_w prior to compression than performance of individual components. Limited restoration in one component (beef, carrots, peas, potatoes) was perhaps less noticeable from a subjective

TABLE I. Effects of Water on Freeze-Dried Foods Compressed after Remoistening to Various Water Activities*

A_w	Chicken (cooked)	Potatoes (cooked)	Beef Stew
0.80	compresses easily; fails to restore at all	-	-
0.70	compresses easily; fair restoration	compress readily but fail in part to resorb and detach	gravy collapsed on other components prior to compression; minimal restoration; gravy hard to wet
0.60	compresses and restores well	compress and restore fairly well	compresses well; all components restore; carrots & peas best; meat sl. tough; potatoes soft
0.50	compresses but disintegrates in part upon rehydration	slices shatter upon compression; some pieces restore	compresses well; components separate well on rehydration; meat tender; peas & potatoes tend to disintegrate
0.40	crumbles upon compression	fragment upon compression; no restoration	peas, potatoes crumble; mixture hard to compress; poor recovery
0.30	fragments upon compression	-	-
0.20	powders upon compression	-	-

*Freeze-dried materials were exposed to atmospheres of these water activities at 25°C. prior to compression at 25°C.

TABLE I (continued). Effects of Water on Freeze-Dried Foods Compressed after Remoistening to Various Water Activities

A_w	Mushrooms (cooked)	Noodles (cooked)	Tuna (cooked)	Tuna-Noodle-Casserole
0.80	essentially no recovery	compress well; fair recovery; tendency to agglutinate	compresses readily; good recovery	good compression of all components; good separation & recovery; noodles tend not to disperse
0.70	very limited recovery	compress well; restore well save for tendency to clump	tends to crack upon compression; good recovery	good compression of all components; good separation & recovery; noodles tend not to disperse
0.60	limited recovery	tendency to break upon compression; fair restoration	tends to break up on compression; pieces recover well, however	definite tendency to crush with loss of identity; less tendency for noodles to clump on rehydration; good recovery
0.50	fair recovery (not complete)	considerable fragmentation; little recovery	fragments during compression; pieces recover well, however	-
0.40	limited recovery	crumbles upon compression	crumbles upon compression; recovers with fair texture	-
0.30	damage upon compression; v.limited recovery	-	-	-
0.20	fragments upon compression	-	-	-

TABLE I (concluded).

A_w	Cottage Cheese	Pineapple	Apple
0.80	recovers slowly to fair texture	-	-
0.70	recovers to good texture	-	-
0.60	recovers to fair texture	-	-
0.50	crumbles upon compression; restores to soft texture	collapses upon resorption; flows upon compression; disintegrates on rehydration	fails to recover in cold water; restores in hot water
0.40	fragments on compression; rehydrates to a paste	disintegrates on rehydration	fair restoration; best in warm water
0.35	-	fragments on rehydration	-
0.30	powders on compression	pieces intact on rehydration; texture soft	recovery excellent in hot or cold water
0.25	-	firm texture on rehydration	-
0.20	-	fair texture on rehydration; pieces tend not to separate	fair to good restoration; best in hot water
0.15	-	some crumbling on compression; fair texture in hot water	compresses but disintegrates on rehydration
0.10	-	crumbles upon compression	crumbles upon compression
0.05	-	shatters upon compression	powders upon compression

TABLE II. Effects of Water on Foods Compressed after Limited Freeze-Drying to Various Water Activities*

A_w	Tuna (cooked, slowly frozen)	Tuna (cooked, rapidly frozen)	Noodles (cooked, both freezing rates)
0.65	compresses readily; excellent restoration; rapid water uptake	compresses readily; excellent restoration; rapid water uptake	flow on compression; poor restoration; pieces tend not to separate
0.50	compresses well; good restoration	compresses well; fair restoration	fair restoration
0.40	compresses well; good restoration	compresses well; fair restoration	fair restoration
0.30	cracks form on compression; fair restoration	cracks form on compression; fair restoration	good restoration
0.20	some crumbling on compression; some restoration	some crumbling on compression; some restoration	poor restoration
0.10	fragments on compression; poor restoration	fragments on compression; poor restoration	fragments on compression; poor restoration

* Water activities were determined at -10°C., that being the temperature at which desorption was conducted; compression was conducted at 25°C., after warming.

TABLE II (Concluded).

A_w	Chicken (cooked, slowly frozen)	Chicken (cooked, rapidly frozen)	Cottage Cheese (slowly frozen)	Cottage Cheese (rapidly frozen)
0.65	poor to fair restoration; pieces stick together	poor restoration; pieces stick together	-	-
0.50	poor to fair restoration	poor restoration	-	-
0.40	good restoration	poor restoration	ready compression; poor restoration	ready compression; poor restoration
0.30	fair restoration	poor restoration	ready compression; poor restoration	satisfactory compression; fair recovery
0.20	fair restoration	fair restoration	fair restoration	good restoration
0.10	tissues crack on compression; fair restoration nonetheless	tissues crack on compression; fair restoration nonetheless	powders on compression; no recovery	powders on compression; no recovery

point of view where other components recovered well. Most persistent among the shortcomings was a tendency for potato to disintegrate in the gravy phase, the latter acquiring the consistency of a heavy paste.

In summary, the several components of the beef stew were observed to restore as well (or, as poorly) in the presence of each other and the gravy solubles as they did in separate tests.

Mushrooms, subjected to 500 p.s.i., were not observed to restore very well in any instance. Good recovery was, however, obtained where compression was limited to pressures in the range 50 to 100 p.s.i. at 0.5 or 0.4 a_w.

Good behavior was observed in glycerolated noodles to span a rather broad range of water activities. Heavier glycerolation (20% vs. 10%) resulted in a compression/recovery performance even less dependent on a_w. Taste of glycerol, however, was determined to be objectionable in the latter case. When less heavily glycerolated noodles were examined, piece-to-piece adhesion appeared to be more of a problem than restoration of individual pieces.

Slowly frozen tuna restored very well indeed. Good recovery was not critically dependent on water activity prior to compression. Tuna judged excellent in texture was obtained from tissues freeze-dried at room temperature and exposed to a_w's of 0.8, 0.7 and 0.6 prior to compression. Tissues subjected to slow freezing and to limited freeze-drying to water activities (at -10°C.) of 0.6, 0.5 and 0.4 likewise restored very well. Rapid freezing prior to limited freeze-drying appeared to reduce the chances of a good recovery (cf. chicken).

Tuna noodle casserole restored very well indeed. Water activities of 0.7 and 0.6 were equally effective in treatment prior to compression. Each component appeared to rehydrate and recover as well in the presence of the others as in their absence.

Good behavior was noted in creamed cottage cheese to center about an adjustment to 0.7 a_w at 25°C. and to 0.3 or 0.2 at -10°C. Rapid freezing prior to limited freeze-drying was, apparently, preferable. In a series of experiments not shown in Table I, dry curd cottage cheese was found to exhibit best behavior following resorption to 0.7 a_w.

Pineapple did not recover well in cold water. Rehydration with hot water, however, resulted in very good restoration (apparently without any loss in flavor). Low water activities were required to achieve best behavior.

Apples restored very well in cold water following exposures to 0.3 a_w prior to compression. Good restoration, less critically dependent on a_w, was obtained when rehydration was performed with hot water. Exposure to hot water, however, resulted in some softening.

3. Organoleptic Evaluation of Rehydrated Materials.

Six foods, prepared in sufficient quantities, were rehydrated for submission to 12-man taste panel sessions. Some foods recovered readily and were examined by the panel. In other cases food slabs 1 to 2 cm. thick proved so resistant to rehydration they were not submitted to the panel. Where foods were not submitted to the panel they were subjected to special examination by the kitchen staff associated with the taste panel operation.

(a) Apples. The difficulties encountered in the rehydration of discs 1.5 cm. thick precluded taste panel tests. Freeze-dried controls, however, rehydrated very readily to a most acceptable texture, slowly frozen material in 3 minutes, rapidly frozen in 2 minutes.

Compressed materials exposed to cold or to very hot water underwent a total disintegration at the outer surface before the innermost areas were completely rehydrated. Intermediate zones of considerable proportion could, at the same time, be said to consist of acceptable material. The problem seemed to reside in a failure to effect a uniformly good recovery.

(b) Beef stew. Slowly frozen, freeze-dried control and compressed materials were rehydrated with boiling water (3 g. per g. dry wt.) for such times as proved necessary, i.e., for 10 to 15 minutes and for 30 minutes respectively. Some parts of some discs especially resistant to rehydration were forcefully separated. The adhesion of the potatoes,

during rehydration, to the other components was particularly noticeable. The products were judged as follows:

Table III

Mean Scores:		
Control, freeze-dried	not compressed	4.5
Resorbed to 0.50 a_w,	25°C., compressed	4.4
Resorbed to 0.60 a_w,	25°C., compressed	4.4
Resorbed to 0.70 a_w,	25°C., compressed	4.5

Significance:

Differences are not significant

(c) Chicken. Freeze-dried controls and compressed materials were restored with a slight excess of boiling water and kept in a hot water bath for 10 to 20 min., sufficient in each case for complete rehydration. Materials derived from slowly frozen chicken were assessed by the panel as follows:

Table IV

Control, freeze-dried,	not compressed	3.5
Resorbed to 0.50 a_w,	25°C., compressed	5.4
Resorbed to 0.60 a_w,	25°C., compressed	5.2
Resorbed to 0.70 a_w,	25°C., compressed	4.9

Significance:

Differences are significant ($p = 0.05$)

Least significant differences: 1.1 ($p = 0.05$)

Materials derived from rapidly frozen chicken were evaluated in a subsequent session as follows:

Table V

Control, freeze-dried,	not compressed	5.7
Resorbed to 0.50 a_w,	25°C., compressed	5.0
Resorbed to 0.60 a_w,	25°C., compressed	4.3
Resorbed to 0.70 a_w,	25°C., compressed	4.6

Significance:

Differences are not significant.

The slowly and the rapidly frozen materials cannot be compared, having been examined by the panel on different occasions. The definite impression was, however, gained that the slowly frozen product restored to a better texture. The rapidly frozen materials were, moreover, less readily hydrated.

(d) Cottage cheese. Since the compressed materials prepared in the form of discs 1 to 1.6 cm. thick did not rehydrate completely in a 1-hour period, they were not submitted to the taste panel. Certain observations were, however, recorded during the various attempts at restoration.

None of the compressed materials was totally resistant to rehydration at 25°C. None of the rehydrated materials, moreover, lost the texture regained on restoration. That is, texture, once recovered, was maintained at 25°C. for periods of from one to three hours. Water entered the discs more rapidly the lower the water activity to which the freeze-dried material was resorbed prior to compression. Slow freezing prior to freeze-drying was more effective in promoting rehydration than was rapid freezing.

Table VI

Extent of Rehydration in 30 min. at 25°C.; Thickness of Dry Core Expressed as Percentage of Original Thickness of Compressed Material

Water activity during resorption prior to compression	Slowly frozen prior to freeze-drying	Rapidly frozen prior to freeze-drying
0.60	20 to 30%	40%
0.70	30%	50%
0.80	40 to 50%	60 to 70%

(e) Pineapple. Slowly frozen materials were rehydrated in 100°C. water without difficulty, drained, cooled and submitted to the panel. Rapidly frozen freeze-dried, compressed products were observed not to rehydrate completely in any instance. The latter samples were therefore submitted only to brief examinations.

Slowly frozen, compressed, restored materials were scored by the panel as follows:

Table VII

Control, freeze dried,	not compressed	4.0
Resorbed to 0.20 a_w,	25°C., compressed	2.8
Resorbed to 0.25 a_w,	25°C., compressed	4.5
Resorbed to 0.30 a_w,	25°C., compressed	4.1

Significance:

Differences are significant ($p = 0.05$)

Least significant difference: 1.1 ($p = 0.05$)

The control rehydrated in seven minutes, those resorbed to 0.2, 0.25 and 0.30 a_w prior to compression, in 25 minutes, 15 minutes, and 11 minutes, respecitvely. The panel commented favorably on the flavor retained in each instance.

Rapidly frozen material resorbed to 0.10 or to 0.20 a_w prior to compression was only partly rehydrated in 30 minutes at 100°C. Very dense, tough, somewhat flexible centers persisted in otherwise unacceptably soft tissues. Material resorbed to 0.30 a_w prior to compression rehydrated in part to yield expanded discs the outer portions of which exhibited very acceptable texture. Dense, tough, innermost zones were, however, also detected. Rapidly frozen control samples, not compressed, rehydrated to an acceptable texture in 10 minutes (cf. 7 minutes for the slowly frozen controls).

(f) Tuna-noodle casserole. Compressed and control materials were rehydrated with boiling water and maintained thereafter at the boiling point for periods of 30 minutes. Portions served to the panel were rated as follows:

Table VIII

Control, freeze-dried,	not compressed	4.9
Resorbed to 0.50 a_w,	25°C., compressed	4.6
Resorbed to 0.60 a_w,	25°C., compressed	4.3
Resorbed to 0.70 a_w,	25°C., compressed	3.6

Significance:

Differences were not significant.

It was observed that the compressed materials all offered some resistance to rehydration. Noodles appeared not to detach from each other. Samples rehydrated to 0.50 a_w prior to compression resorbed with the least difficulty.

4. Water Sorption Studies, Equilibrium, Quantitative.

(a) Resorption isotherms, obtained subsequent to conventional freeze-drying.

The resorption data are presented in the form of 11 curves denoting the binding of water by freeze-dried materials exposed to atmospheres of precisely controlled

water activity. The plots are seen in Fig. 8 to 17, inclusive, and are indicated in each case by the letter "R." All the resorption plots were obtained from foods frozen slowly prior to freeze-drying, except where indicated.

(b) Desorption isotherms.

These are shown in Figs. 9, 10, 13, 14, and 16; they are indicated in each case by the letter "D." These data represent the extents to which the freeze-dried materials continued to bind water after limited freeze-drying to the various water activities indicated. Only in one case did the freezing rate appear to effect the course of the desorption isotherm. Only in pineapple (Fig.14) was the resorption isotherm observed (quite unexpectedly) to cross the desorption isotherm.

One notes very considerable relative displacements of the curves "D" and "R" in most cases and, in certain cases, distinct differences in shape. The relative displacements in the cases of chicken and tuna are of similar form.

(Note: After desorption at -10°C. to 0.70 a_w, the specimens were in each case desorbed not to 0.60 a_w as originally intended but to 0.66 a_w. An error made in calculating the required sample temperature/condenser temperature difference was not detected until after the series of desorption experiments was completed. Subsequent stepwise desorption was in each case accomplished according to plan.)

(c) Special study: construction of a "virtual desorption isotherm."

The extent to which the activity of the water retained during desorption increases with increased temperature is illustrated in Fig. 18.

These effects from changing temperature are indicated by the unbroken line, the direction of the changes in water activity, weight, and temperature, by the arrows. The "virtual desorption isotherm" obtained from freeze-dried beef at room temperature (23°C.) was obtained by joining those points representing water activities assumed by the sample when warmed at various water contents from -10 to 23°C.

This latter "isotherm" is represented by a line of long dashes. A line of short dashes indicates the course of direct desorption conducted entirely at -10°C. (curve reproduced from the previous Final Technical Report). Similarly, a dotted line indicates the course of resorption at 25°C.

One notes the behavior of the sample during the repeated desorption/warming/cooling sequences to be much closer to the direct desorption at -10°C. than to the resorption at 25°C. One notes also that water released by the specimen on warming (from A to B for example) is regained readily when the specimen is cooled again to -10 (B to C) but that it is released a second time (C to D) when the sample is caused once more to adjust to the water activity maintained previously at -10°C. Desorption from D to E clearly follows very nearly the course described by direct desorption, at -10°C., in experiments in which the sample was <u>not</u> subjected to intermittent warming.

5. Rate Determinations.

(a) Freeze-drying at room temperature.

Measurements of the rates at which apple, beef-stew, chicken, cottage cheese, pineapple, and tuna-noodle casserole freeze dry at room temperature are reproduced in Figures 19 through 24. The data points denote the places where measurements were taken from continuous recordings obtained during each experiment.

One notes that rapidly frozen chicken freeze-dried to a lower solids content than did the slowly frozen product. One notes also that cottage cheese freeze-dried to different solids contents depending on the preparation. Both chicken and cottage cheese freeze-dried at rates comparable with those obtained in the Phase I studies on beef and shrimp.

Tuna-noodle casserole freeze-dries as rapidly as do chicken and cottage cheese despite the presence of components rich in starch.

Apples, pineapple, and beef-stew, by contrast, freeze-dry much less rapidly.

(b) Humidification velocities.

The times taken by the various foods freeze-dried at room temperature to resorb water from the vapor phase may be judged from the weight/time recordings obtained during exposure of each freeze-dried food to that a_w required for best compression/restoration behavior. Figures 25 through 30 describe the uptake of water, from the vapor by freeze-dried apple, beef-stew, chicken, cottage cheese, pineapple, and tuna-noodle casserole at 25°C. Times taken to regain nine-tenths of the water eventually resorbed varied from 3, 5.5, 6, and 7 hr. for chicken rapidly frozen, slowly frozen, beef-stew and cottage cheese, respectively, to 15, 16, and 20 hr. for tuna-noodle casserole, apple, and pineapple.

(c) Final drying velocities, after compression.

Since the weight/time plots describing the drying of the compressed materials were obtained from the samples employed to measure humidification velocities prior to compression, the corresponding curves have been plotted together (again Figs. 25 to 30, inclusive).

Chicken desorbed very rapidly; apple, beef-stew, and tuna-casserole somewhat less rapidly, appearing reluctant to release the last 0.5, 2.5 and 1.0 g. water per 100 g. dry product, respectively.

Pineapple was observed to undergo final drying from the compressed state with extreme reluctance.

6. Operation of Pilot-scale equipment for limited freeze-drying.

The apparatus illustrated in Figs. 6 and 7 (see also Methods, p. 10) was subjected to several careful tests and trial runs. The temperatures of the air in the cold room, the surface of the sample chamber, and the coolant surrounding the condenser were observed to fluctuate 0.8, 0.1 or less, and 0.1 deg. C., respectively. Clearly, the cyclic fluctuations in the air temperature were damped by

the mass of the metal assembly. Successful continuous control of sample chamber/condenser temperature difference to ±0.05 deg. C. further demonstrated the constancy of the sample chamber temperature.

Pressure rise tests showed the system to be essentially free of leakage. When the condenser was primed with ice, and temperature and temperature difference maintained in an otherwise empty system, the isolation of the sample chamber/condenser assembly from the vacuum pump/pressure throttling system did not result in a visibly increased pressure reading in a 10-hour period. Neither did the pressure in the sample chamber undergo a measureable change in a similar period when the latter part of the system was further isolated from the condenser. Since change in pressure greater than 10 microns could be detected quite readily the rate of leakage into the system could not have been in excess of 0.10 micron-liters per hr. (based on a measured system volume of 15 liters — 10 for the sample chamber, 5 for the condenser).

Some indications of the performance of the set-up, under load, were obtained during a test run with a typical, well-defined material. Frozen peas, free-flowing and free from excess ice, were packed one layer deep on each of five shelves (250 ± 10g frozen material being accommodated per shelf). The peas were subjected to limited freeze-drying such that the water activity tended to 0.40; the room was kept throughout at -10°C; the condenser was arranged to maintain a temperature 9.0 deg. C. lower than the sample chamber.

Periodically the apparatus was opened and the tiers (shelves, spacers, retainers, and contents) were weighed at -10 (in the same room) without disturbing the arrangement of the sample. On each occasion, freeze-drying was reestablished within 30 minutes. When it was clear that dehydration had progressed to constant weight the peas were removed to the bench at 25°C. where they were further dried over freshly baked Linde Molecular Sieve in vacuo.

Table IX presents the course of the drying, at -10, to 0.40 a_w. Water content (g water per 100g solids) is listed according to the shelf and the duration of the process. Clearly, the ice was sublimed from the peas in 120 hours, or less.

TABLE IX. Pilot-Scale Studies on Frozen Raw Peas (av. dia. 10 to 11mm.). Water Contents during Limited Freeze-Drying to 0.40 a_w at -10°C. (expressed as g. water / 100g. dry wt.).

	Time (hrs.)							
Shelf*	0	24	67	94	120	144	168	192
1	391	298	162	87	38	15	12	11
2	387	303	171	98	43	17	10	8
3	386	305	175	98	44	17	11	8
4	387	304	168	91	37	11	9	8
5	390	255	101	41	17	10	9	9

*Shelf #1 uppermost; shelf #5 nearest condenser (see Fig.7).

The water vapor pressure measured above the product on the topmost shelf was found to fall, first slowly, then to reach 0.9mm Hg rather rapidly (1.5, 1.5, 1.5, 1.4, 1.3, 1.0, 0.9, 0.9, 0.9mm, on successive days). Apparently the process was in part "mass-transfer limited." Larger connections and/or a larger condensing surface would most probably, have rendered the process "heat-transfer limited," effecting as much as a threefold increase in the drying rate.

Several additional runs in which various quantities of other foods were subjected to limited freeze-drying at -10°C. were completed without difficulty. Ease of assembly, operation, and disassembly were repeatedly demonstrated.

7. Additional Compression/Restoration Studies: Three Foods, Four Freezing Rates.

Each of three cooked foods was frozen at -10, -30, -78, and -196°C. (see Methods) to furnish materials having markedly different internal structures. Each of the twelve types of sample thus obtained was freeze-dried at room temperature to a very low water content. Beef was resorbed, prior to compression, to water activities of 0.3, 0.4, 0.5, 0.6, and 0.7, chicken to 0.4, 0.5, 0.6, 0.7 and 0.8. Carrots were resorbed to water activities of 0.4, 0.5, 0.6, and 0.7.

Quantitative measurements of the effects of exposure to 500 p.s.i. (for 1 min.), the time to rehydrate (in hot water), also the extent of the ensuing recovery were obtained in each instance from several samples. Brief visual inspection of the measurements showed that the results were not, in general, statistically significant. Here and there, however, certain trends became apparent.

It appeared, for example, that in beef the most deleterious compression resulted from the combination of high freezing rate with highest water activity. No correlation was, on the other hand, obtained between freezing rate and time to rehydrate after compression.

Carrots were rather clearly less resistant to compression, the higher the freezing velocity. Higher cooling rates also caused (i) less rapid, (ii) less extensive recovery from compression at 0.4 and 0.5 a_w.

Chicken was, likewise, less rapidly rehydrated the higher the freezing rate. A corresponding tendency to less nearly complete recovery was, however, not detected.

8. Restoration of Compressed, Solvent-Extracted Material.

The results of physical compression/restoration studies conducted on various solvent-extracted materials are summarized in Table X. Behavior is listed with reference to water activity prior to compression.

Slowly frozen, freeze-dried, solvent extracted cooked beef recovered best when adjusted to 0.60 a_w prior to compression.

(Similar studies completed during the first phase of this work revealed a uniformly fair restoration dependent on pretreatment at water activities at 0.20, 0.30, 0.40, 0.50, 0.60 and 0.70. Solvent extracted materials derived from rapidly frozen cooked beef were, however, observed to recover best when first exposed to water activities of 0.50, 0.60 and 0.70).

On the basis of earlier observations, the best a_w for solvent-extracted cooked beef would appear to be 0.15 units higher than that for control cooked, freeze-dried beef.

TABLE X. Effects of Water on Freeze-Dried, Solvent Extracted Foods Compressed after Remoistening to Various Water Activities

A_w	Beef (cooked)	Chicken (cooked)	Apple (fresh)	Pineapple (canned)
0.80	compresses v. readily; poor restoration	compresses v. readily; poor restoration	compresses v. readily; fair restoration	compresses v. readily poor restoration
0.70	compresses readily; fair restoration	compresses readily good restoration	compresses readily; good restoration	compresses readily; fair restoration
0.60	compresses readily; good restoration	compresses readily; fair restoration	compresses readily; fair restoration	compresses readily; poor restoration
0.50	compresses readily; fair restoration	compresses with some breakage; fair restoration	compresses readily; poor restoration	compresses readily; poor restoration
0.40	compresses readily; fair restoration	shatters on compression; pieces show fair restoration	compresses readily; v. poor restoration	compresses readily; poor restoration
0.30	compresses with some breakage; fair restoration	crumbles on compression; no restoration	compresses readily; v. poor restoration	compresses readily; v. poor restoration
0.20	shatters on compression; no restoration	powders on compression; no restoration	compresses readily; no restoration	compresses readily; no restoration

Cooked chicken subjected to slow freezing, freeze-drying and solvent extraction recovered best when resorbed to 0.70 a_w prior to compression, that is, to a water activity 0.10 units higher than that found best for cooked freeze-dried material not subjected to lipid extraction (Tables X and I, respectively).

Apple extracted with aqueous ethanol recovered best when exposed to 0.70 a_w prior to compression, less well at 0.60 and 0.80, and very poorly at 0.50 and lower values. Such performance stands in marked contrast to that of fresh apple tissue which, when frozen and freeze-dried, recovered best when exposed to 0.30 a_w prior to compression.

Solvent-extracted pineapple made a somewhat less impressive recovery than apple. Much as in apple, however, a large change in best a_w was observed to accompany solvent extraction. Best a_w was, that is, raised from 0.25 to 0.70.

9. Cytological Studies.

(a) Cooked beef (Photos. 1 through 10).

Slowly frozen tissues subjected to freeze-drying and rehydration but not to compression differed very little in appearance from cooked controls. Fibers failed, however, to regain their initial cross-sectional areas. Freeze-drying appeared, therefore, to reduce the water holding capacity of the individual fibers.

Greatest damage was observed on rehydration when compression followed exposure to 0.20 a_w. Fibers were fractured and displaced. Little obvious damage was detected in tissues exposed to 0.50 a_w prior to compression. In specimens resorbed to 0.80 a_w, compressed and rehydrated, fibers were aggregated apparently from fiber-to-fiber adhesion resulting from compression.

In parallel studies, rapid freezing prior to freeze-drying was found to permit still better recoveries. With the exception of the specimens compressed at 0.20 a_w the structures on rehydration were hardly distinguished from the cooked controls (Photos. not included).

(b) Cooked chicken. (Photos. 11 through 20)

Exposure to freezing, freeze-drying and rehydration altered the appearance of the fiber contents but did not result in physical damage.

Compression at 0.40 a_w resulted in considerable damage; neither fibers nor connective tissues regained their initial form on rehydration. Compression at 0.60 a_w resulted in reduced damage; compression at 0.80 a_w seemed to be still less harmful. Best behavior was not, therefore, correlated with an intermediate a_w though water activities were chosen after completion of other studies.

In a corresponding series of observations on cooked chicken subjected to rapid freezing, the freeze-dried control and the samples exposed to 0.40 and 0.60 a_w prior to compression recovered somewhat better than did the slowly frozen ones. Rapidly frozen samples compressed at 0.80 a_w recovered less well (photos. not included).

(c) Canned tuna. (Photos. 21 through 30).

The greatest observable changes in tuna appeared to result from freezing and freeze-drying. Fibers were markedly condensed; they lost, in part, their ability to recover, i.e., to hydrate to the original level and acquired a brittle quality. Connective tissues were observed to form a striated coagulum.

Compressed materials exhibited better recovery the higher the a_w prior to compression. On the basis of appearance only the damage due to compression may be summarized:

$$\text{damage } (0.40\ a_w) > \text{damage } (0.60\ a_w) > \text{damage } (0.80\ a_w)$$

Rapidly frozen materials were not examined.

(d) Apples (Photos. 31 through 40).

Very little damage was immediately apparent in any specimen. Cellular arrangements were excellently retained in materials subjected to freeze-drying and to rehydration and in rehydrated specimens exposed to 0.40 a_w prior to compression. Further inspection, however, revealed a near

absence of intercellular spaces in all specimens subjected to compression.

Breaks in the cell wall appeared here and there in 0.20 and 0.60 a_w-compressed materials. Greater tendencies to recover (or to assume) rounded shapes were noted in materials exposed to 0.60 a_w prior to compression. Elongated cells suggestive of flattened structures were seen to persist more frequently in specimens compressed at 0.20 and 0.40 a_w. None of the compressed, restored specimens was, however, distorted in the plane perpendicular to the direction of compression.

(e) Pineapple (Photos. 41 through 50).

The canning process seemed not to affect the structure of the tissue save perhaps to cause cell walls to break occasionally. Freezing and freeze-drying resulted in more extensive damage. Cell walls were broken in greater numbers. A partial collapse resulting from freeze-drying was, moreover, not completely reversed by rehydration.

Compression/restoration treatments did not seem to contribute to further damage at 0.25 a_w. Tissues exposed to 0.40 a_w prior to compression were, however, found to retain impressed configurations upon rehydration.

10. Scanning Electron Microscopic Studies.

Four types of sample were examined in the scanning microscope at magnifications from 20× to 10,000× and depths of focus several hundred times those achieved in other types of microscope at corresponding magnifications. Freeze-dried, compressed and freeze-dried, solvent extracted, compressed raw beef were compared with freeze-dried and freeze-dried solvent extracted controls, respectively, and with each other.

Evidence of an original freezing pattern was obtained from control preparations, not compressed. Freezing patterns were, however, entirely absent from compressed materials. The course of compression was found to depend on the water activity prior to compression, but not on solvent extraction. Subsequent remarks on whole and solvent extracted materials are thus recorded with reference to water activity.

(a) Compression at 0.20 a_w.

Both extracted and unextracted materials subjected to 500 p.s.i. (Photos. 51 and 52, respectively) exhibit, in general, considerable numbers of irregularly shaped empty spaces. Bounding the latter, fibers generally possessed irregular cross sections and appeared to make face-to-face contact in isolated instances only. Little or no evidence was found for plastic flow within the fibers during compression.

(b) Compression at 0.50 a_w.

Pressures of 500 p.s.i. caused the larger spaces between the fibers to disappear, almost without exception (Photos. 53, 54, and 57). Cross sections exhibited polygonal patterns (especially Photo. 57) strongly suggesting an accommodation to the space available. Small spaces, mostly triangular, were however detected wherever three fibers came in contact with each other. Resistance to distortion, that is, to relative displacement of fiber contents and/or to changes in fiber surface area, was therefore indicated.

Certain of the spaces apparent in the freeze-dried compressed structures most likely arose in "final drying" during which the fibers very probably underwent slight separation. Such spaces could, however, be distinguished from those not eliminated during compression on the basis of the shapes assumed by the fibers involved (see again Photo. 57).

(c) Compression at 0.80 a_w.

One minute exposures to 500 p.s.i. resulted in the total elimination of free spaces from solvent extracted and from whole, freeze-dried tissues. Very narrow spaces seen in Photo. 55 (but not in Photo. 56 due perhaps to the fiber direction) suggest shrinkage and detachment during final drying.

Disproportionately frequent observation of elliptical and otherwise elongated cross sections among the fibers (where they were clearly distinguished) suggested a deformation of the fiber far in excess of that required to fill

the polyhedral voids. Rather it appeared that the specimens were, during compression, subjected to massive shear and to macroscopic, possibly plastic displacements. Solvent extracted materials in this instance appeared to be less deformable than tissues from which lipids were not removed.

To summarize, the findings under the microscope were correlated with decreased resistances to compression determined by physical tests. Detailed descriptions of the various extents to which spatial relationships were altered were obtained. Solvent extraction prior to moistening and compression had little effect.

DISCUSSION

The several separate studies just reported have been grouped for the purposes of discussion into three categories. Thus, the significance of the results will be considered with reference (1) to the small scale production experiments, (2) to the pilot-scale practice and (3) to the theory of the processes related to compression. Inasmuch as the methods employed were, for the most part, discussed in some detail in the previous Final Technical Report, detailed analyses of the laboratory procedures have been omitted.

1. Compression/Restoration Behavior.

(a) One component systems. An analysis of the results of the laboratory compression/restoration tests (Tables I and II) and a comparison of the latter with the verdicts returned by the taste panel (Tables III, IV, V, VII and VIII) require discussion with reference to water content at time of compression. The properties of the various single foods are thus examined with reference to the relevant sorption isotherms (Figs. 8 through 10, 12 through 16), as follows:

(i) Apples. Best restoration was observed in apples compressed after resorption to 0.30 a_w. Thus, from the resorption isotherm, the water content for best restoration was 0.050 g./g. dry tissue. Such a value compares with 0.045 g./g. for peach (from the previous F.T.R.) and 0.035 to 0.050 for pineapple. (This report, page 45)

These best water contents are so much lower than those required in plant tissues less rich in sugar and in other foods that it seems worth the while to consider the possible cause of the differences. To a first approximation the freeze-dried plant tissue can be viewed as a two-phase, two-component system composed of cellulose and sugar. On exposure to water the sugar phase, doubtless amorphous after freeze-drying, sorbs more water than the cellulose. Given a high enough a_w, the sugar phase softens and flows under stress, the cellulosic phase deforming simultaneously, with reluctance.

Since the sugar-rich phase flows only above its glass transition temperature, the sugar/water ratio has to be decreased to cause the latter to fall below the temperature selected for compression. Where the system is moistened further, the sugar-rich phase may flow too readily, the various internal surfaces being annhilated in the process. The cellulosic component may, moreover, lose its ability to retain a strained form at high water activities, the sugar and the excess water plasticizing the irreversible deformation.

The restoration observed where apples were placed in hot water tends to support such a hypothesis. Irreversible deformation might prove reversible where sufficient energy (i.e. heat) was available.

The failure of the thicker slabs where single pieces gave a good performance calls for close attention. Evidently a way must be found to permit water to reach each piece in the slab. Similar problems arose in several other foods in the present study; practical suggestions are presented in a subsequent section.

(ii) Chicken. Good restoration was obtained from slowly frozen chicken compressed after direct desorption, also after resorption from dryness. That is, recovery was not dependent on the avoidance of, or the passage through certain states of dryness prior to compression. The good recovery demonstrated by chicken frozen slowly prior to limited freeze-drying and to compression may, however, be contrasted with the poor recovery shown by chicken compressed after rapid

freezing and limited freeze-drying. Clearly, the freezing rate was a most important factor.

The strong dependence of the best recovery of the slowly frozen chicken on water activity prior to compression may be traced, through the appropriate isotherm, to dependence on water content. Both desorption and resorption isotherms are seen to be very steep in the regions in which best behavior was observed; that is, best restoration was very strongly dependent on water content.

It is, however, also quite clear that the water content best after limited freeze-drying (0.140 g./g. dry tissue) differed from that required (0.105 g./g.) when dry material was resorbed at 25°C. It would appear that, where the protein has been exposed to drying, a lesser quantity of water suffices to render the tissue deformable. One must suppose that the water bound during resorption does not have access to the sites occupied during desorption or, at least, that the sequence according to which the sites are occupied is not obtained by reversing the sequence in which the sites were vacated during desorption.

The taste panel judged desorbed materials compressed at 0.50, 0.60, and 0.70 a_w equally good in each case. The panels' opinions thus coincide, inasmuch as the mean value proves to be 0.60, with the results of the physical tests. The panels' observation that the rapidly frozen material restored less well is also most interesting. It is perhaps especially interesting that the rapidly frozen material restored at all when dried and resorbed when it failed (during physical tests) to restore when prepared by limited freeze-drying.

(iii) Cottage Cheese. Equally good recovery by slowly frozen, resorbed and rapidly frozen, desorbed dry curd cottage cheese contrasts with the fair recovery demonstrated by the slowly frozen desorbed product. No other food was found to offer better restoration after rapid freezing. Possibly these observations reflect the granular nature of the cottage cheese and the disorder characteristic of the denatured protein present.

From the desorption and the resorption isotherms obtained from the dry curd product, the strong dependence of the best behavior on a_w can be traced to best water contents in the range 0.10 to 0.12 g./g. dry material regardless of the freezing rate or the form of the subsequent treatment. Apparently the water molecules are not distributed according

to a pattern determined by the state from which the moist condition was approached.

Further clues to the mechanism may be found in the observation that the dry curd and the creamed cottage cheese products, each slowly frozen, freeze-dried and resorbed, restored best at the same a_w. It would appear, in this connection, that the cream does not reside in places critical to compression or to restoration. The problems involved are therefore seemingly related to the behavior of the proteins present.

The difficulties arising from the need to secure the rehydration of slabs of useful thickness introduces other more practical questions, discussion of which is reserved for a later section.

(iv) Mushrooms. The absence of a really adequate performance at any water activity would appear to originate in the rather elaborate form of the fresh material. In addition to enclosing in part a series of empty spaces, fresh mushrooms contain considerable quantities of air. Proteins, sugars, minerals and fibers are present in the ratio, roughly, of 3 : 4 : 1 : 1.

The best recovery, obtained at 0.50 a_w, requires, according to the resorption isotherm, a water content of 0.050 g./g. dry tissue. Probably the water acts in two ways, first to soften the sugar/mineral glass, second to soften the protein/fiber matrix. Most likely, compression results in extensive internal surface to surface adhesion not reversed on rehydration.

Possibly the incorporation of an additive to prevent direct surface to surface contact of the various parts of the mushroom would help. Canned mushrooms, not examined in this study, also deserve serious consideration. Their obvious resilience appears, in retrospect, to their potential advantage.

(v) Noodles. When the best water contents are determined from the respective sorption isotherms, one sees the resorbed material restores best when compressed at water contents much higher than those making possible best performance by direct desorption (arrows in Fig. 13). In contrast, the freezing rate prior to freeze-drying does not influence the behavior. According to expectation, the addition of glycerol was observed to lower the best water activity. Glycerol

was also observed to broaden the range of useful water activities. In the absence of additional determinations, it is not known whether glycerol lowers the best water content.

Several factors require further examination. Tendencies to regain volume and texture might be distinguished from tendencies for piece to piece adhesion. The first and second factors are most likely susceptible to considerable manipulation on the basis of existing knowledge of the properties of starch gels and the effects of different thermal treatments in various sequences. The problem of adhesion is perhaps better discussed with reference to the possible effects of additives and/or edible coatings.

(vi) Pineapple. The very good recovery observed in hot water contrasts with its near absence in cold water. While it is still impossible to distinguish the reasons for the marked difference in behavior the poor performance in cold water is very likely related to the adhesion of the cell walls, one to another.

The strongly a_w-dependent behavior in hot water recalls the similarly strong dependence where apples were restored in cold water. The resorption isotherm indicates a best water content of 0.040 to 0.050 g./g. dry tissue, suggesting, as it did in apples, the mediation of a concentrated aqueous sugar solution during compression, the cellulosic component being but slightly hydrated.

The rating accorded frozen material resorbed at 0.25 and 0.30 a_w suggests the potential of the pineapple as long as restoration is induced in hot water. The scores further demonstrate the lack of adverse effect resulting from brief exposure to high temperatures. Clearly the slowly frozen pineapple was difficult to damage!

Rapid freezing was, in comparison, very deleterious. None of the rapidly frozen compressed material prepared for the panel was restored after 30 minutes in hot water. Since rapidly frozen controls were readily rehydrated, one concludes that the rapid freezing in combination with the compression was harmful. In the absence of any positive correlation (1) of rapid cooling with intracellular freezing, (2) of slow freezing with intercellular ice formation, further discussion is beside the point.

Similarly, pineapple collapsed during limited freeze-drying was not restored, indicating, perhaps, very extensive self-inflicted compression. Moderately low temperatures, high-water activities and long times of exposure appeared to act together to cause the total disappearance of the channels created during freezing, possibly also the accommodation of the cellular components in new strain-free states.

(vii) Potatoes. While partial restoration was obtained with potatoes compressed at water activities in the range 0.50 to 0.70; that is, at water contents from 0.060 to .160 g./g. (see Fig. 15), difficulties encountered demand special discussion.

Crumbling during compression, attributed to a too-dry state, was observed to extend to water contents high enough to permit an irreversible adhesion generally attributed to a too-moist state. One problem was not overcome, that is, with change in water content, before another made its appearance. Additives employed in low concentration in processed, sliced potatoes resulted in only moderately improved behavior. Probably the crumbling persisted in the starch at water activities at which cell to cell adhesions was already problematical.

Satisfactory solutions might be found in the selection of especially young potatoes. Alternatively, cooked potatoes subjected to a suitable thermal treatment prior to freezing might acquire a sufficiently durable structure. Methods might have to be devised to permit the effective introduction of small additive molecules into freshly sliced materials.

(viii) Tuna. Most remarkable, perhaps, were the widths of the ranges within which desorbed and resorbed tuna demonstrated good recovery with reference to water activity. Brief inspection of the relevant sorption isotherms (see Fig. 16) shows correspondingly wide ranges in permissible water content (from 0.110 to 0.220 g./g. dry tissue) independent, more or less, of the way in which the water contents were achieved.

Equally remarkable, good recoveries were in fact obtained from water contents where tissues cracked when compressed one piece at a time. Restoring forces released in tuna during rehydration must be very strong.

Somewhat less acceptable restoration resulting from rapid freezing seems to follow the pattern observed in chicken. In tuna, as in chicken, rehydration would appear

to require the opening of channels in the protein phase. Greater internal surface areas resulting from the freeze-drying of the rapidly frozen material were most likely eliminated more readily during compression than those, fewer, larger cavities resulting from slow freezing. Smaller spaces, once destroyed, were, furthermore, less readily redeveloped.

(ix) In Summary. One could question the need to discuss compression/restoration behavior with reference to water activity. Brief consideration of the foregoing analysis of the behavior of single food products shows, however, the usefulness and the limitations of the water activity approach. Clearly, best behavior was defined in each case in terms of a_w in the absence of any knowledge of the water contents involved. Preparation for compression, was, moreover, conducted in equipment in which a_w's were, one way or another, predetermined.

In contrast, a knowledge of best water content permits preparation for compression only by direct admixture, one way or another, of food product and water.

With a knowledge of the best a_w and the sorption characteristics (i.e. the isotherm) one is free to select any preparative method. Notwithstanding these alternatives, it is the composition that appears, very largely, to determine the physical properties. Thus a knowledge of water contents is essential (either way) to any discussion of the molecular basis for the best behavior.

Desorption isotherms appear to be of particular value inasmuch as direct desorption to predetermined water contents at any of a variety of freeze-drying temperatures may prove desirable.

Figure 31 depicts a series of desorption isotherms describing the dependence of the water content on a_w (referred always to liquid water) at each of a series of sub-freezing temperatures (A.P.MacKenzie, data to be published, plotted in the form first employed by Riedel, Kaltetechnik, 13, 122-128, 1961).

Clearly, the same water content (w) is achieved by limited freeze-drying to a lower a_w, the lower the freeze-drying temperature. To produce a material having a predetermined water content best for compression at 25°C. one would necessarily employ a greater sample temperature/condenser temperature difference the lower the freeze-drying temperature. The driving force resulting in heat transfer would, that is,

have been increased. Possibly, the limited freeze-drying at the lower temperature (-20°C. for example) would yield a sample of a desired water content sooner than a corresponding limited freeze-drying at -10°C. The possibility deserves serious consideration.

It was, on the other hand, observed in the course of this and other studies that best restoration required the preparation of material of higher water content the lower the temperature at which the compression was to be conducted. Figure 32 describes the requirements where the compression was, for one reason or another, conducted at the freeze-drying temperature. Superimposed on the series of isotherms presented first in Figure 31 is a curve depicting the dependence of the best moisture content on the temperature at which the compression is carried out.

Here the situation is somewhat different. Compression at the lower temperature, requiring the higher water content demands a less extensive desorption; that is, a decreased sample/condenser temperature difference during limited freeze-drying. In such circumstances, the highest permissible freeze-drying temperature is indicated.

(b) Mixed Food Products — compression of resorbed material.

Interesting problems arise in mixed foods where each component exhibits best performance at an a_w and a water content characteristic of that component. Further interest attaches to the modification of the best water activities where substances originating in one foodstuff penetrate another. Similarly the effects of various added substances command attention. The two mixed food products examined in the course of this study are, as far as possible, examined from these points of view.

(i) Beef stew. It is of special interest that the best performance of the five-component mixture was determined by physical test and by the taste panel to depend less on a_w prior to compression than did the several components in separate tests. If these judgments reflect accurate objective analyses it is likely that, in the processing of the mixture, each component is affected by the presence of others to the benefit of the respective components' abilities to recover. If, on the other hand, improved acceptance results from decreased discrimination by the panel, the benefits attached to the preparation of mixed food products are not be minimized.

The compatibilities of the components employed to make the beef-stew can be judged from Figure 33 (with the understanding that the improved acceptance is apparent), the data being gathered from isotherms previously described in this and the first Final Technical Report. Such plots as Figure 33 could prove helpful to further discussion. Modifications bringing best a_w's for beef and peas closer together are, for example, indicated in the present instance.

Best performances are, moreover, clearly insufficient in certain cases. Beef and potatoes, the latter especially, call for further examination.

Additional studies will be required before the effects of the substances released by one component on the performance of another can be determined. Tendencies for certain component surfaces to interact and adhere should also be examined in greater detail.

(ii) Tuna casserole. While the physical tests showed the recovery to be excellent at 0.60 and 0.70 a_w, the taste panel judged the materials compressed at 0.50 and 0.60 a_w to be preferable to those compressed at 0.70 a_w (an informal assessment despite the absence of a true statistically significant difference). Probably the difference in best a_w relates to the difficulties encountered in the rehydration of the larger slabs compressed at the higher a_w's. Adhesion seems to be reversed less easily, the larger the sample. Partial fragmentation resulting from compression at lower a_w aids, in contrast, in the creation of the pathways by which water penetrates the larger samples.

Since the tests showed the various components to recover as well (but no better) in the presence of each other than in their absence, further discussion can, it appears, be conducted with reference to the resorption isotherms obtained from the various separate components. From the composite plot (see Figure 34) the mushrooms are seen to exhibit the lowest optimum a_w and the greatest a_w-dependence, that is the steepest isotherm. A more compatible mixed food product would result, were it possible to lower the best a_w's of the noodles and the tuna (the freeze-dried white sauce matrix would, in the process, be less likely to soften and collapse). A search for ways to raise the best a_w for the mushrooms, or to flatten the mushroom isotherm, would, on the other hand, perhaps serve equally well. It is sufficient at this stage to point out the various possibilities.

(iii) In Summary. It is evident that foods can be matched with reference to the dependence of the properties of each on a_w to permit the formulation of mixtures capable of uniformly good recovery after compression. Inasmuch as consumers appear less critical, perhaps, of the performance of components in admixture than of the same foods taken one at a time, the matching process is facilitated.

Sources of water of predetermined a_w were shown to provide effective means of preparing mixed freeze-dried materials for compression. From the desorption isotherms and the composition of the mixture the weight of water resorbed could be calculated in advance where such information was desired.

The resorption isotherms describing the behavior of the single foods permit the determination of the components most usefully retained, eliminated, or modified. The modification of the properties of individual components appears, in particular, to offer a rather promising means of obtaining (or improving) useful mixtures.

(c) Compatibility, one food with another, by limited freeze-drying.

The activity exerted at some higher temperature by the water remaining after limited freeze-drying was easily determined — specimens subjected to limited freeze-drying were merely permitted to warm in an enclosed space free from air. The virtual desorption isotherm obtained from beef indicates the extent of the increase in a_w and the dependence of the former on the degree to which the sample was first desorbed. In the absence of evidence to the contrary the stepwise procedure by which the virtual desorption isotherm was obtained is thought to be valid though, to be correct, a separate specimen should be used to provide each point.

Specimens subjected to limited freeze-drying together to a single a_w at, say, -10°C., might, after warming, exhibit (1) similarly increased a_w's, (2) a_w's increased to different extents.

In the first of these instances no redistribution of water would occur. That is, a mixture compatible with respect to compression/restoration behavior on the basis of water contents achieved by limited freeze-drying would still be compatible after warming (each component in the

presence of the others). In the second instance the free energy differences arising on warming would initiate a redistribution of the water remaining in the food after limited freeze-drying. Food components exhibiting larger-than-average increases in a_w would, presumably, desorb according to virtual desorption isotherms. Components undergoing complementary resorption would regain weight in accordance with applicable "scanning isotherms," the latter originating from the respective "virtual" desorption isotherms. Scanning isotherms, functions of the substrate and the lowest water content achieved during desorption, necessarily originate from, and are located between the virtual desorption isotherm and the corresponding isotherm describing resorption from dryness.

Figures 35 and 36 illustrate the possibilities. They have been drawn to indicate the nature of the work involved in the rational selection of those components compatible during compression at, say, 25°C. when the mixture was subjected to limited freeze-drying at, say, -10°C. Semi-empirical determinations of best mixtures by limited freeze-drying might, however, prove to be both useful and less time consuming.

(d) Significance of approach. It was assumed, in the foregoing discussion, that the significance of the results was not affected by the size of the batches employed in the course of the study. In this connection, the following factors must be borne in mind.

(i) It is likely that "freeze-drying at room temperature" probably provided materials of better quality than did the average commercial process.

(ii) The "humidification" was observed to be nearly isothermal; that is, the results of the vapor phase remoistening were not a function of the sample size as they might have been with larger loads.

(iii) It is probable that the behavior during compression was representative of that of larger quantities except where the lateral motion during the compression of the smaller quantities was not prevented.

Studies on the restoration of individual pieces did not provide information with reference to the separation of the pieces, one from another, or their detachment from massive

blocks during rehydration. More extensive experiments are indicated in certain cases.

2. Further Practical Considerations.

(a) Rates. The rate determinations would appear to contribute useful information. Specifically the freeze-drying rates helped to distinguish the food products less willing to freeze-dry, less willing, that is to permit the diffusion of water (since the heat transfer was, it would appear, about equally good in each experiment).

The measurements of the rates at which materials resorbed water, via the vapor phase at 25°C., demonstrated the practicality of "moistening by resorption." The plant tissues rich in sugar resorbed much less rapidly than the protein foods, confirming the conclusions presented with the previous Final Technical Report. The resorption measurements very likely indicate also the upper limits of rates of equilibration where liquid water is added directly to food (the water must still penetrate each part of each component). A discussion of other factors determining the distribution of the water added directly to freeze-dried foods is, however, not within the scope of this report.

The measurements of the rates of final desorption indicate the times required for the final drying of slabs several mm. thick. The finite nature of the rates in question should not be discounted.

The freeze-drying and resorption rates were perhaps more dependent on the experimental geometry than the desorption rates. The former involved large changes in the temperature of the sample in comparison with sample chamber/condenser and sample chamber/evaporator temperature differences, respectively. Specimens cooled during final desorption but little in comparison with sample chamber/condenser temperature differences.

(b) All metal pilot plant apparatus. The successful operation of the pilot-scale unit demonstrated heat and mass transfer according to expectation in an apparatus capable of duplication on a larger scale. The usefulness of the design was evident from the ease experienced in the assembly, operation and disassembly and in the cleaning of the apparatus.

In the form in which it was tested the set-up would require the insertion of silicone o-rings between the components of the vacuum system, also the thermal insulation of the electric motors prior to continuous operation at -20, -30 or -40°C. Such steps were unnecessary at -10°C.

The need for constant ΔT rather than constant condenser temperatures where the specimen chamber temperature varied cyclically was discussed in the first Final Technical Report. Maintenance of constant sample chamber/condenser temperature difference can be defined with reference to what is now known regarding the dependence of desorption isotherms on temperature (A.P. MacKenzie, paper in preparation). Thus, while the sample chamber temperature did not vary during the test experiments, cyclic variations with attendant (in phase) variations in condenser temperature would not preclude successful operation. Clearly, questions relating to temperature control assume a greater importance the larger the equipment.

3. Theoretical Aspects.

(a) Variation in freezing rate prior to compression.

(i) Cooked beef. The decreased restoration exhibited by the beef frozen in liquid nitrogen suggests failure of the water to penetrate the collapsed labyrinth within the fibers (previous studies have shown the highest of the freezing rates employed to cause a growth of hundreds of separate ice crystals inside each fiber). Since, during compression, the physical displacements within the fibrillar matrix are clearly less extensive the higher the freezing rate the failure to rehydrate is, perhaps, best attributed to tendencies on the part of the intracellular surfaces to mutual, irreversible adhesion.

(ii) Carrots. The lesser resistance to compression detected in the more rapidly frozen carrots can best be explained in terms of freezing-freeze-drying hysteresis. The large distortion introduced during freezing very likely results in a physically stronger matrix, softening on resorption notwithstanding. A reduced recovery detected in the carrots frozen at the higher velocities (a marginal difference, to be sure) could be linked, as in beef, to greater tendencies to adhesion, one surface to another, within the compressed

structure. The greater resistance to compression accompanying the slower freezing most likely reduces the incidence of the surface to surface adhesion. The problem seems to be compounded by rapid freezing in that it results (1) in greater internal surface area, (2) states from which the surfaces thus created are more likely to meet.

(iii) Chicken. The complete recovery of the rapidly frozen chicken despite the better compression, can only be explained in a manner consistent with the previous arguments in terms of a reversible adhesion (cf. beef). Possibly the better behavior is associated with the lower lipid content, or with ultrastructural differences. A reduction in the rate of recovery with increased freezing rate is presumably the direct result of the subdivision of the routes available for the re-entry of water.

(b) Solvent extraction.

(i) Beef. Table XI summarizes the combined description of the whole foods (Table I) and of the corresponding solvent-extracted materials (Table X). The present work confirms the conclusions drawn from the previous study that the best a_w was raised 0.15 water activity units by solvent extraction. It would seem that the lipids do contribute to the adhesion of the component surfaces, one to another, within the compressed material. In their absence, the supposed adhesion requires a more extensive moistening (and softening) of the protein.

(ii) Chicken. An increase in best a_w with solvent extraction somewhat less marked than that in beef correlates with the known low lipid level in light chicken muscle. Corresponding studies on dark meat would seem to be indicated.

(iii) Apples. Table XI shows the very extensive shifts in best a_w resulting from the extraction of the sugar-rich plant tissues. Evidently apples behave much the same way as peach (see the previous report). Most likely the sugars bind sufficient water at low a_w's to plasticize the cellular matrix and, at higher a_w's, to permit the total elimination of the spaces by which water might return. The cellulosic structures themselves are, by contrast, much less prone to bind water. Only at 0.7 a_w do they appear to soften sufficiently to deform without physical rupture.

TABLE XI. Comparison of the Performance, on Rehydration, of Whole and Solvent-Extracted Compressed, Freeze-Dried Tissues.

(G = good; F = fair; P = poor)

a_w:	0.20	0.30	0.40	0.50	0.60	0.70
Beef, cooked, slowly frozen, whole :	P	F	G	G	F	P
Beef, cooked, slowly frozen, extracted :	P	F	F	F	G	F
Beef, cooked, slowly frozen, extracted* :	-	F	F	F	F	F
Beef, cooked, rapidly frozen, extracted* :	-	F	F	G	G	G

* data from the previous Final Technical Report.

a_w:	0.30	0.40	0.50	0.60	0.70	0.80
Chicken, cooked, slowly frozen, whole :	P	P	F	G	F	P
Chicken, cooked, slowly frozen, extracted :	P	F	F	F	G	P

(continued)

TABLE XI (Concluded). Comparison of the Performance, on Rehydration, of Whole and Solvent-Extracted Compressed, Freeze-Dried Tissues.

(G = good; F = fair; P = poor)

a_w:	0.20	0.30	0.40	0.50	0.60	0.70	0.80
Apple, fresh, slowly frozen, whole :	F	G	F	F	-	-	-
Apple, fresh, slowly frozen, extracted :	P	P	P	P	F	G	F

a_w:	0.20	0.25	0.30	0.40	0.50	0.60	0.70	0.80
Pineapple, canned, water pack, slowly frozen, whole :	F	G	F	P	P	-	-	-
Pineapple, canned, water pack, slowly frozen, extracted :	P	-	P	P	P	P	F	P

(iv) Pineapple. While the best performance after solvent extraction was never better than "fair," the best a_w was shifted to a higher water activity than it was in apple; that is, the best a_w was raised very considerably. Probably the same arguments apply. The plasticizing effects of the sugar solutions developed when the glass-like regions resorbed water would seem to claim a place in any discussion of the restoration of compressed plant tissues.

Table XII lists the fiber and the sugar contents of the plant tissues discussed in this and the previous report (Watt and Merrill, 1963). Among the tissues richer in sugars the best recovery (admittedly in hot water) was observed in the tissue lowest in fiber content, having the highest sugar/fiber ratio. Excellent recovery was, however, obtained from the cooked carrots having the highest fiber content and the lowest sugar-fiber ratio. Much remains to be learned.

Table XII

Food	Sugar	Fiber	Ratio	Recovery	Best a_w
Apple, fresh	13.5	0.6	22:1	Good	0.30
Peach, fresh	8.5	0.6	14:1	Very poor	0.30
Pineapple, canned	9.9	0.3	33:1	Excellent	0.25
Cabbage, fresh	4.6	0.8	6:1	Very poor	0.35
Carrot, cooked	6.1	1.0	6:1	Excellent	0.55

(c) Cytological Studies.

(i) Beef, cooked. Cytological studies support in some respects the findings of physical compression/restoration studies. Evidence of fiber breakage resulting from compression was observed in the restored specimens compressed at 0.20 a_w and, in small measure, in those compressed at 0.50 a_w. While no fiber breakage was seen in the specimens compressed at 0.80 a_w, fiber aggregation was detected; that is, fibers

brought into contact failed to separate upon rehydration. A decreased water binding resulting from freeze-drying (in specimens not compressed at all) was also detected. Improved compression/restoration behavior thus depends to some extent upon improved response to freeze-drying and/or to final drying (it would not be difficult to distinguish the separate effects of the two last-named treatments). Possibly, final drying could be limited to a reduction to a water activity (hence to a water content) measureably greater than zero.

(ii) Chicken. In contrast with beef, chicken "control" specimens, freeze-dried and rehydrated, appeared to regain their original size and form; fibers were equally large; spaces between fibers were correspondingly small. Such observations correlated well with the taste panel's informal opinions of the respective control materials.

The steadily increased performance of the compressed, rehydrated chicken with increased a_w did not correlate with the observation that the chicken recovered best when compressed at 0.60 a_w. The very long times during which the tissues were rehydrated and fixed prior to transfer to paraffin wax may, however, have permitted a time-dependent restoration not noticed in tests limited to 30 minutes, or thereabouts. These observations call into question such terms as "irreversible damage."

(iii) Tuna. The lack of any sharp dependence of good recovery on a_w prior to compression is borne out by the microscopic study. In this respect, tuna is shown to be the least a_w-dependent muscle tissue, chicken being more dependent, beef much more so. Presumably the tuna muscle tissue is less brittle at lower a_w, less adhesive at higher a_w. In the absence of a detailed comparative study, one can only speculate as to the cause of the different behavior. Possibly the behavior of the tuna is to be traced to the extensive distribution of non-fibrillar material, this being the most obvious of the differences visible under the microscope.

(iv) Apples. The lack of obvious damage to the restored apple tissues is of little direct help in determining the causes of the failure to restore. The micrographs do not, however, indicate the absence of a turgor pressure, nor do they necessarily indicate the original structure prior to fixation. Probably the prolonged exposure to water and, afterwards, to fixative, results in restoration in excess of that achieved in a shorter test.

The absence of the extracellular spaces in the compressed, rehydrated tissues depends, presumably, on the nature of the surfaces turned toward the spaces. Inasmuch as a system composed of such interconnecting spaces might constitute a "natural" route to rehydration the nature of the cell's surface is of considerable interest.

(v) Pineapple. Despite the suggestion that the freeze-drying itself results in some damage, the pineapple demonstrates a remarkable power to recover in hot water. The vascular bundles recover especially well, together with the cells surrounding them. The tendency on the part of the flimsy cellulosic framework to resume its original size and shape in the presence of so much sugar could result from a resilience inherent in the fiber structure. A tendency for water to enter damaged cells at a rate many times that at which sugars could diffuse away would, however, have the same effect. Doubtless the absence of an osmotic response could be demonstrated.

(d) Scanning electron microscopic investigations.

Evidently muscle tissue was very well suited to scanning electron microscopic examination. In-depth views of internal surface structures revealed considerable information not readily gathered in other ways. Apparently, the preparative methods employed permitted the creation and the maintenance of surfaces indicative of typical internal structures.

At 0.20 a_w, that is, at 4.0 g. water/100 g. dry tissue, the whole and the solvent-extracted raw tissues were clearly too stiff to demonstrate plastic rearrangements. Surface contours impressed during freezing remained after compression, preventing fiber-to-fiber surface contact and attainment of high bulk densities. Exposure to 0.50 a_w prior to compression (rehydration, that is, to 9.0 g. water/100 g. dry tissue) appeared, on the other hand, to soften the fiber contents sufficiently to permit limited changes in fiber cross sections during a 1 minute compression. Compression at 0.80 a_w (that is of tissues containing 20 g. water/100 g. dry tissue) was, in contrast, shown to proceed with changes in the shape of the fibers corresponding to that degree of gross distortion that allowed the specimens to fill the space remaining in the chamber.

Possibly the extra resistance in solvent extracted specimens was due to (1) denaturation of the protein during

the solvent extraction with an attendant decreased water resorption, (2) absence of any plasticizer within the fibers, (3) absence of a plasticizer between the fibers.

Best recovery seems to depend on a moisture content high enough to permit a limited plastic deformation during compression. Too-dry systems cannot be compressed. Very moist systems rearrange too readily during compression; small spaces are completely eliminated; fiber-fiber adhesion is facilitated.

Where intimate fiber-fiber contact was not effected, final drying appeared to result in a fragmentation of the compressed specimens, the spaces created being distinguished by their size and shape etc., from those remaining after compression. Channels suitable for rehydration were, that is, created during final drying. Where compression was conducted at too-high moisture contents specimens did not fragment during final drying. Possibly the final drying plays an important part in this respect in the preparation of specimens demonstrating best recovery.

CONCLUSIONS

1. Best recoveries are most usefully defined in terms of water activities to which separate foodstuffs are adjusted prior to compression.

2. Foods can, in most cases, be prepared for compression by direct desorption or by remoistening from a too-dry state with equal ease and effectiveness. Freeze-dried foods appear to desorb and/or resorb water via the vapor very rapidly.

3. Knowledge of the relevant sorption isotherm permits the determination of the best water content prior to compression, corresponding to the best a_w.

4. Rational choice of foods destined for compression in admixture can only be made on the basis of water activity, compression at which yields best recovery in the case of each projected component.

5. There is little or no reason to doubt that information gained from the small-scale experiments presented herewith cannot be used as a basis for large-scale operations.

6. Freeze-drying by sublimation of ice and direct desorption of a portion of the water remaining unfrozen (limited freeze-drying) appears to offer certain practical advantages. The method seems to be well-suited to pilot-scale studies in certain instances.

7. The freezing rate appears in some cases to determine the recovery of the freeze-dried compressed material. Foods high in fats or sugars recover better when first frozen slowly. Foods rich in protein but devoid of fat seem to recover better when frozen rapidly.

8. Physical damage to structural components appears to determine failure to recover from compression at too-low water activities.

9. Lipids are rather clearly involved where freeze-dried muscle tissues fail to recover from compression at higher water activities.

10. Sugar content per se does not seem to determine extent of best performance of freeze-dried, compressed plant tissues. Rather the failure to restore appears to be related to the nature of substances of higher molecular weight.

SUGGESTIONS FOR FURTHER WORK

1. Scientific.

(a). Further studies are required on the effects of different pressures for different times, different pressures at different water activities (i.e., at different water contents) and different pressures (at same or different water content, for different times) at different temperatures.

It is likely that irreversible changes occurring during compression could be reduced not only by selection of best water content — the subject of this study in large part — but by supplementation with acceptable chemical substances. Fresh tissues are penetrated only by certain compounds of lower molecular weight. Substances of higher molecular weight could be incorporated into cooked foods.

It is especially likely that certain foods retain power of good recovery, upon compression, only to certain bulk densities less than 0.80. Possibly different minimum bulk density requirements should be set for different foods, depending on the properties of the food.

(b) The difficulties encountered in the detachment of the food, one piece from another, during the rehydration of food bars of useful thickness requires special attention still. Single foods might be coated with substances capable of rapid resorption and dissolution. Alternatively, food pieces might be freeze-dried from dispersion in solutions yielding cellular matrices crumbling on compression at those a_w's best for the foods themselves. That is, the deliberate use of an "incompatible" matrix may provide a means of preventing the complete elimination of internal surfaces during compression and final drying.

(c) The formulation of mixed food products might be re-examined with particular reference to the compatibility of the components on the basis of a_w. Lowest acceptable a_w's at the time of compression should be determined with special care. Lowest a_w's would result in least times to resorb water after conventional freeze-drying, least times to desorb again during final drying, and better rehydration of thicker slabs. Lower a_w's would also permit more rapid limited freeze-drying.

2. Technological.

(a) It would appear that there is a real need to develop novel methods by which compression might be employed to form the products into shapes most suitable for rapid rehydration.

For example, corrugated molds might be used to prepare compressed material in thin corrugated layers. Such layers could then be pressed together (in a second operation, at a lower pressure and/or a different water activity) to leave grid-like patterns of empty spaces beneficial to final drying and to re-entry of water, with minimal effect on the final bulk density.

(b) Special attention might be devoted to the development of equipment in which desired a_w's could be generated and established and maintained constant from point to point during equilibration and, afterwards, during transfer from freeze-drying apparatus or from humidifier to compression apparatus

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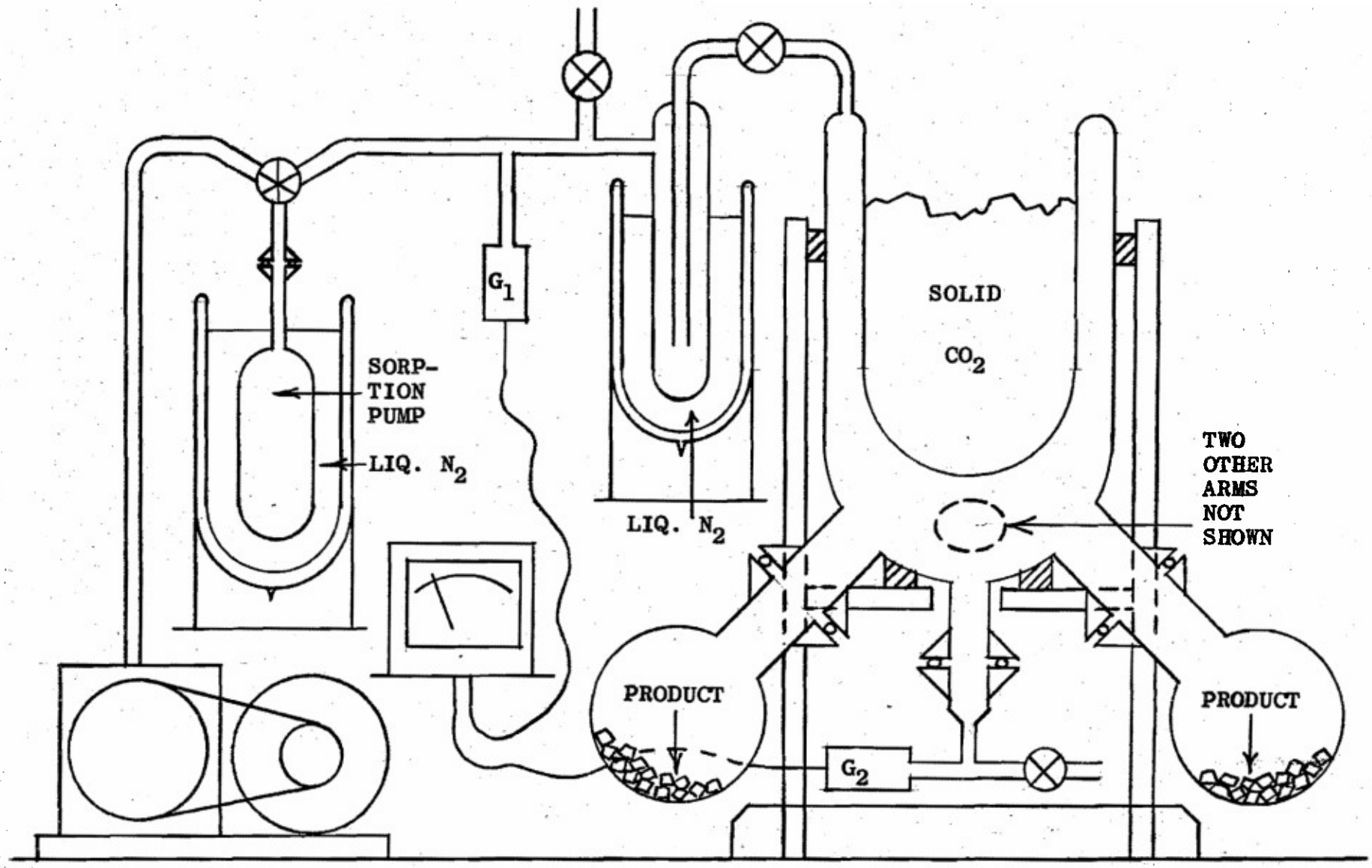


FIGURE 1. APPARATUS FOR CONVENTIONAL FREEZE-DRYING

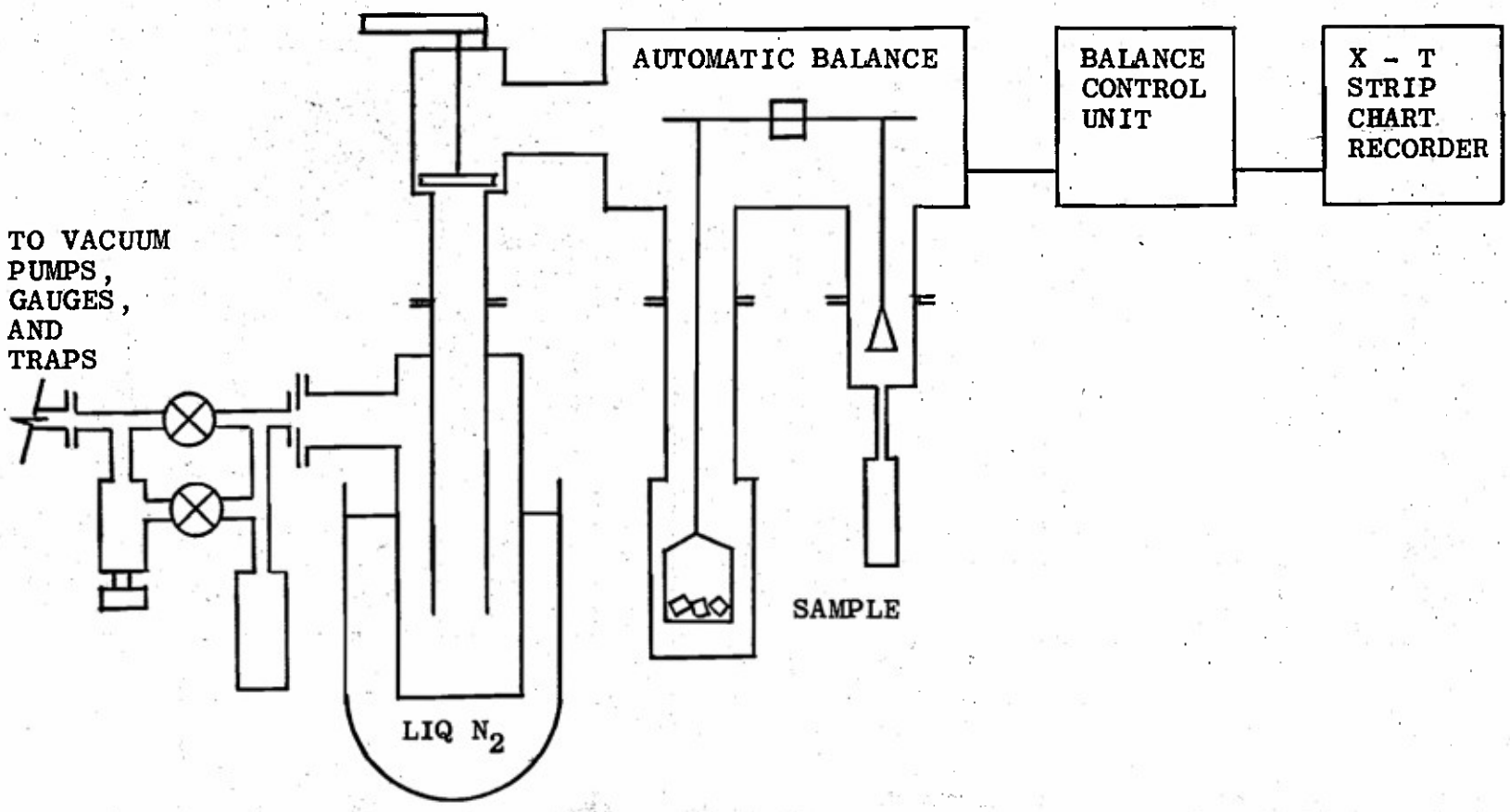


FIGURE 2. APPARATUS FOR THE DETERMINATION OF FREEZE-DRYING RATES.

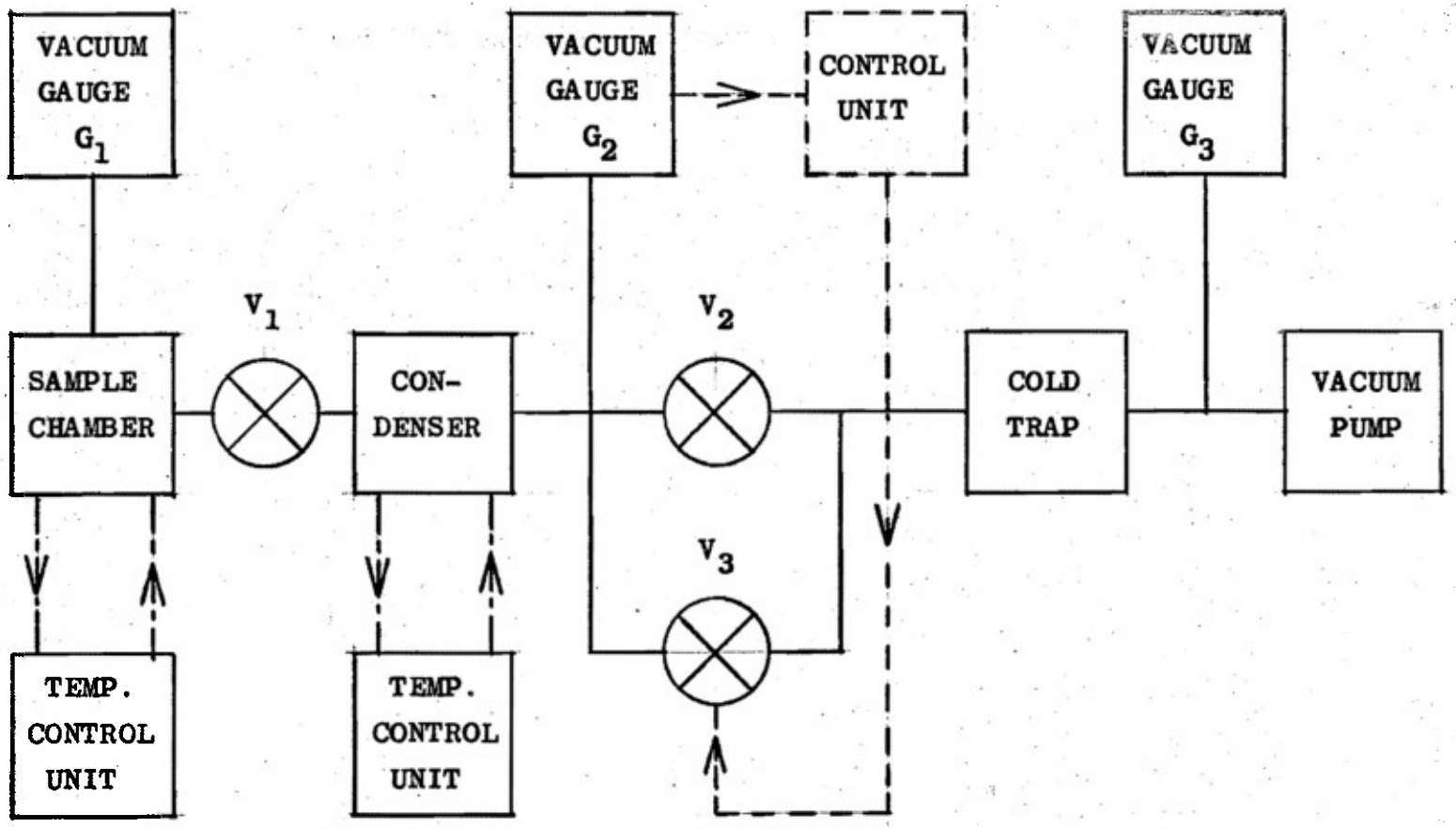


FIGURE 3. DESCRIPTION OF PARTS AND RELATIONSHIPS REQUIRED FOR LIMITED FREEZE-DRYING.

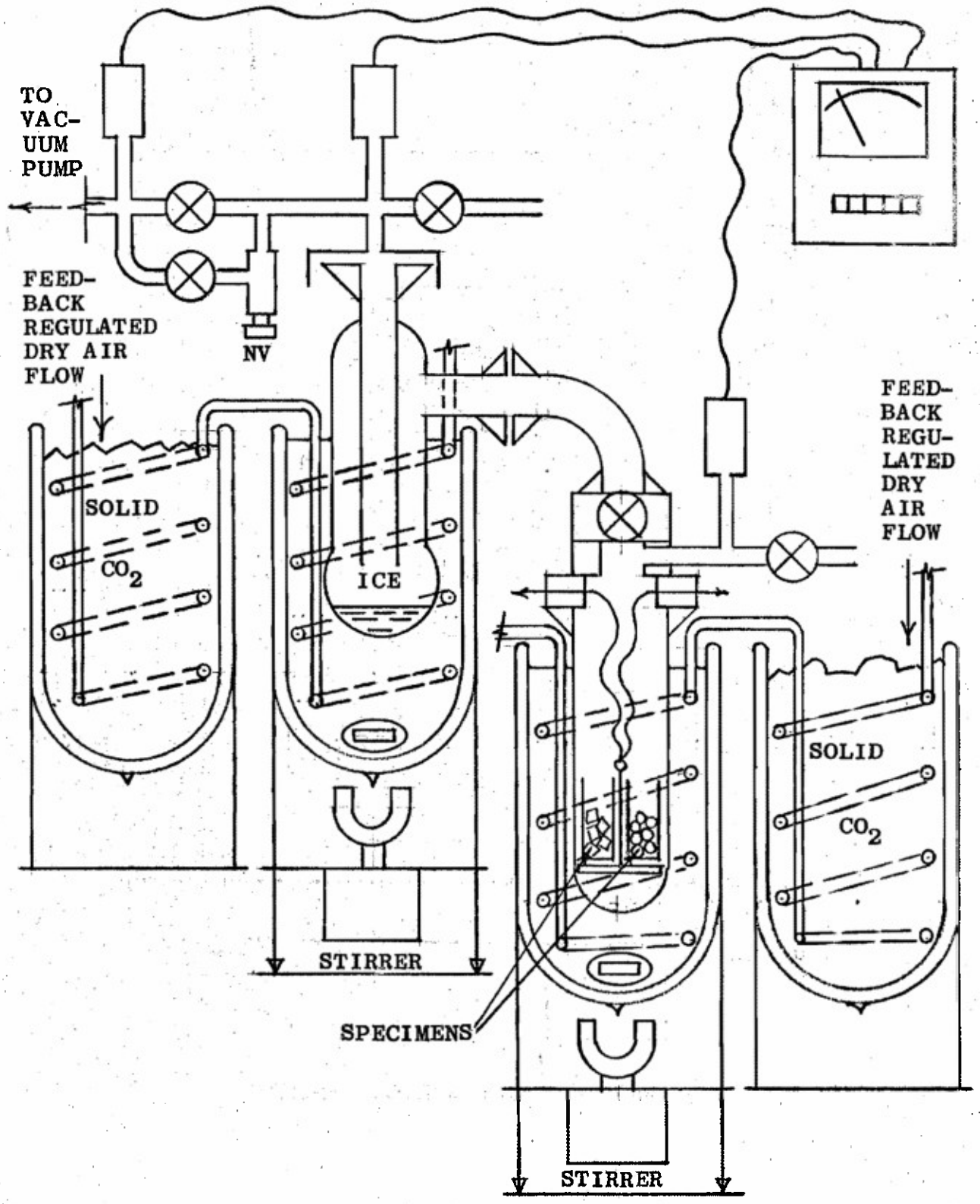


FIGURE 4. APPARATUS FOR LIMITED FREEZE-DRYING.

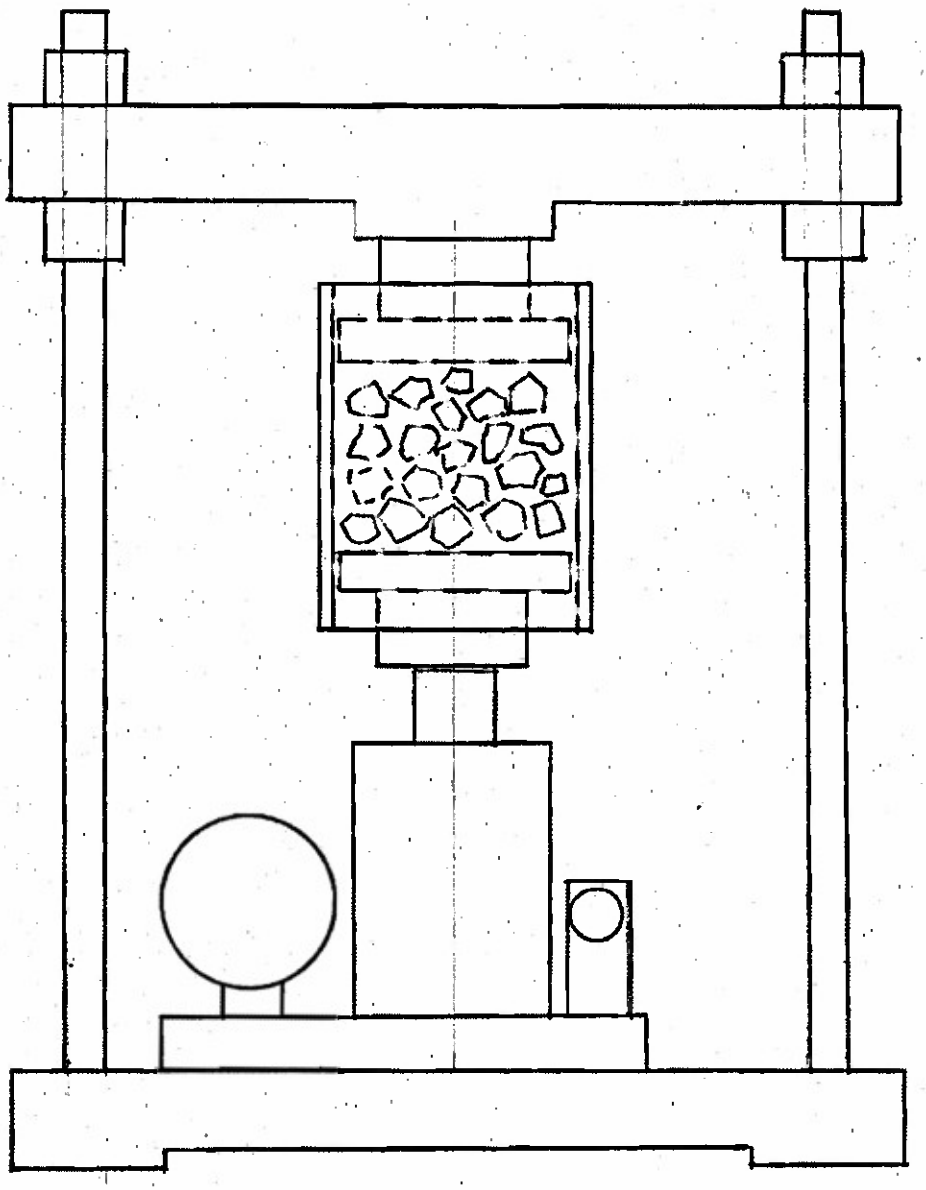


FIGURE 5. COMPRESSION ASSEMBLY

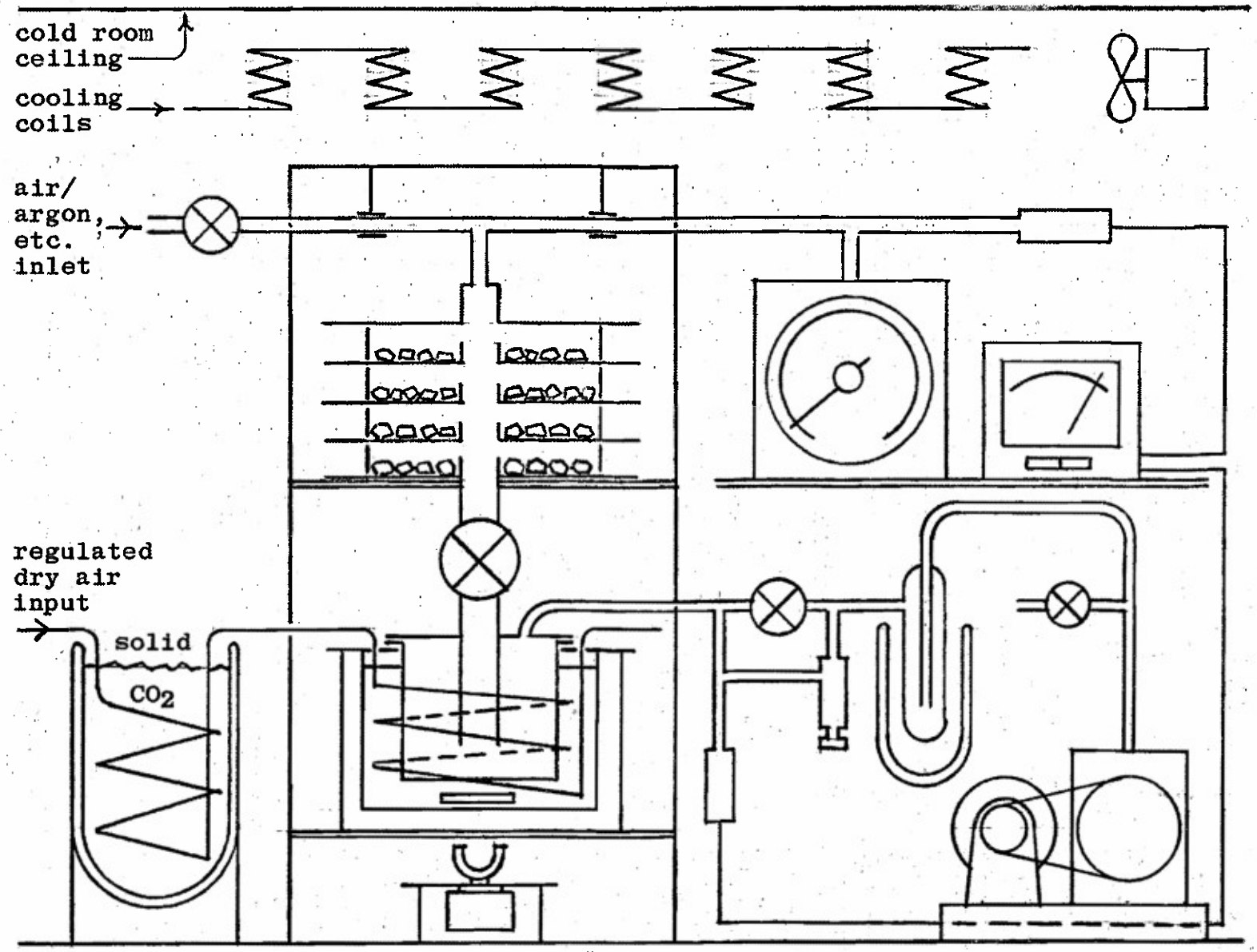


FIGURE 6. ALL-METAL PILOT-SCALE APPARATUS FOR LIMITED FREEZE-DRYING

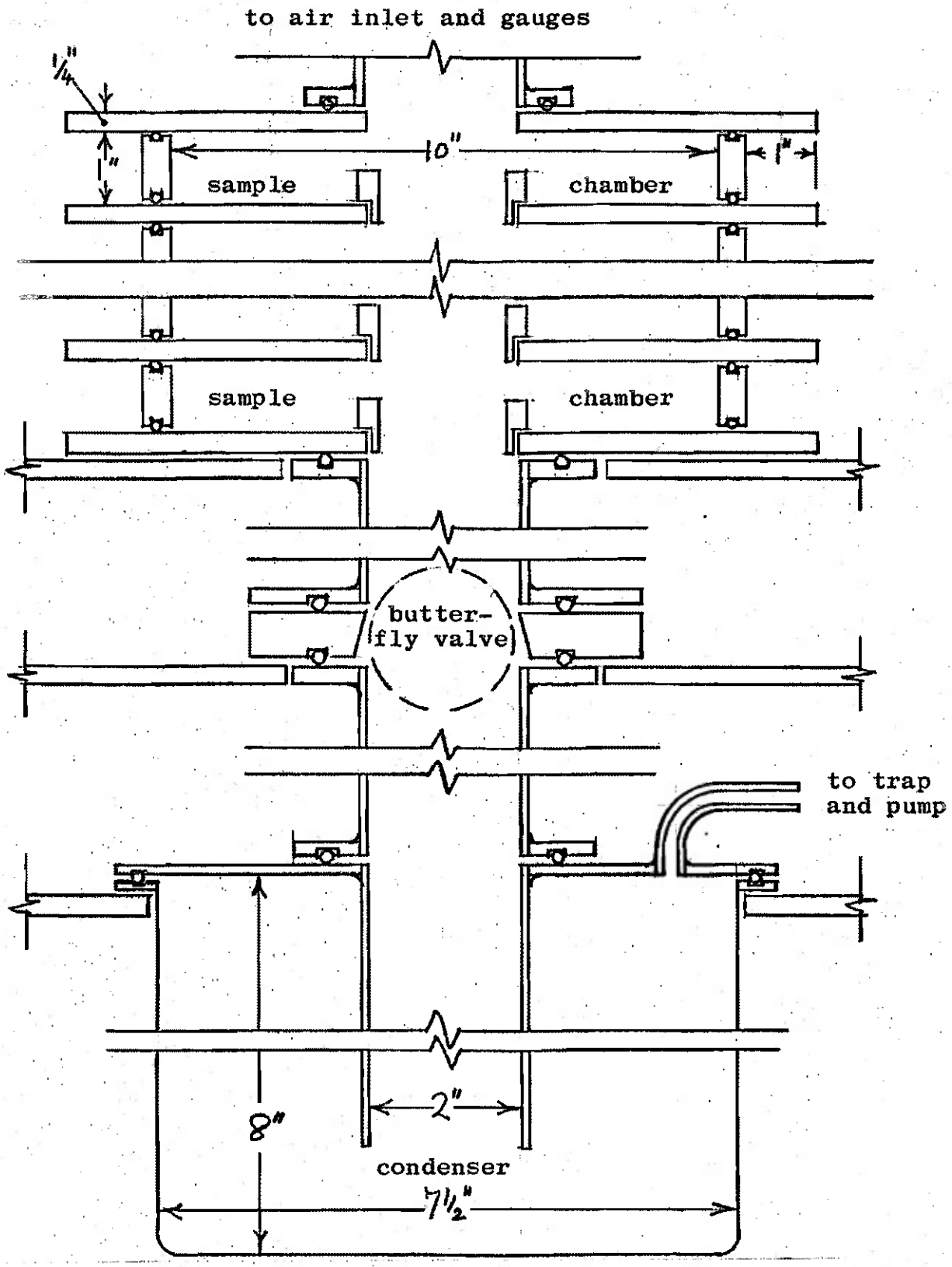


FIGURE 7. ALL-METAL APPARATUS FOR LIMITED FREEZE-DRYING; VACUUM ENGINEERING DETAILS.

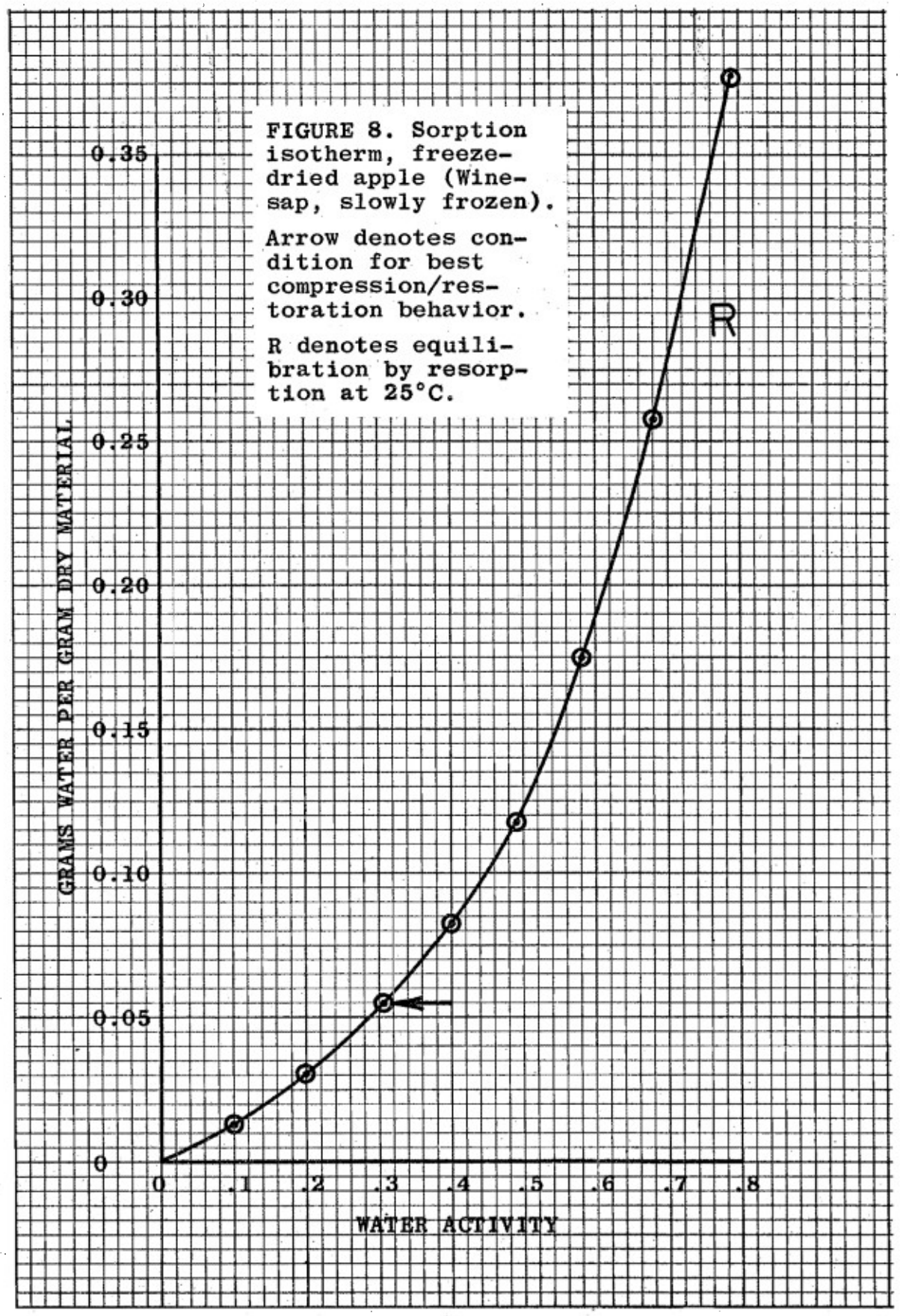


FIGURE 8. Sorption isotherm, freeze-dried apple (Winesap, slowly frozen).

Arrow denotes condition for best compression/restoration behavior.

R denotes equilibration by resorption at 25°C.

FIGURE 9. Sorption isotherms, freeze-dried cooked chicken.

Circles indicate data from slowly frozen samples; crosses indicate data from rapidly frozen samples.

Arrows denote conditions for best compression/restoration behavior. (R) and (S) denote freezing rates.

D denotes equilibration by direct desorption at -10°C; R denotes equilibration by resorption at 25°C.

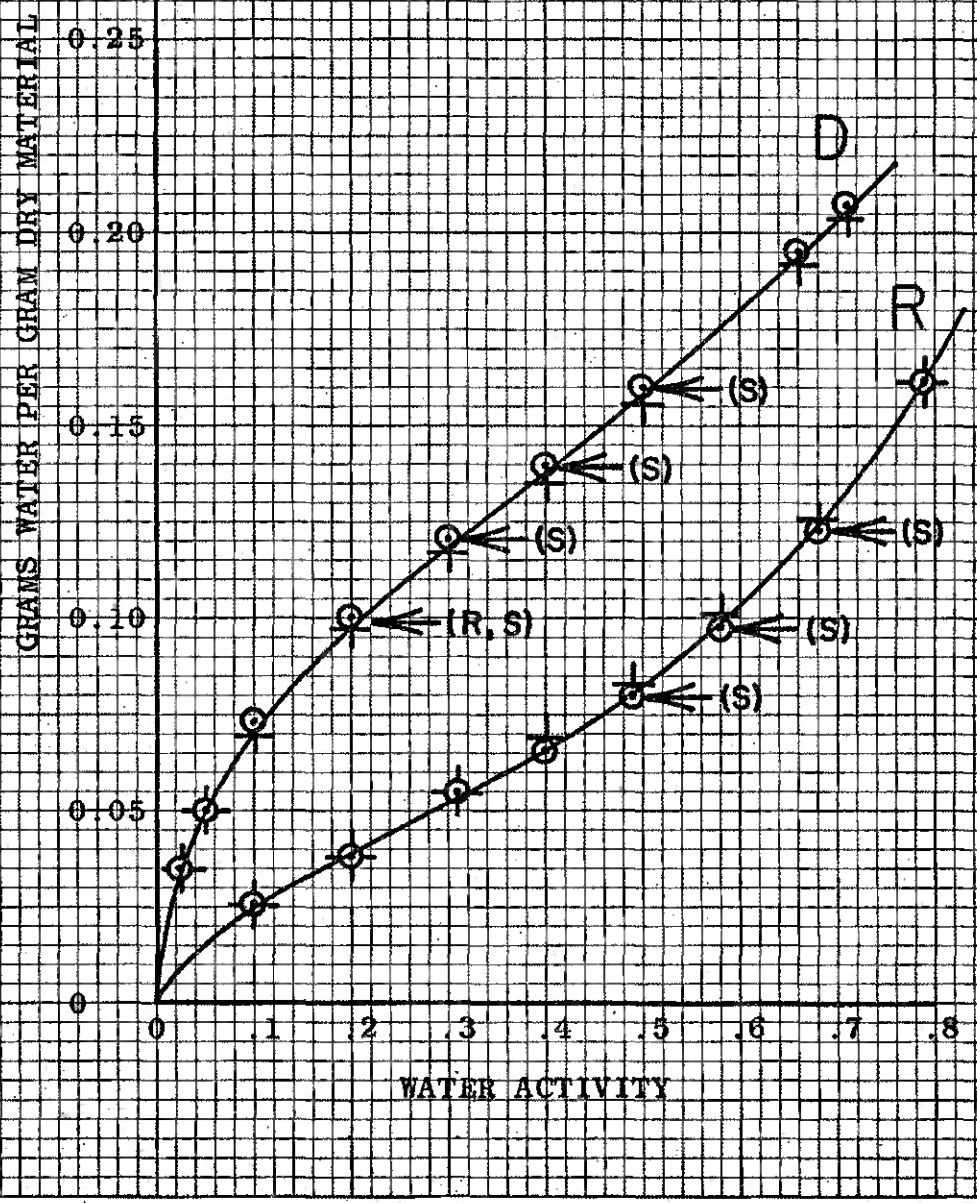
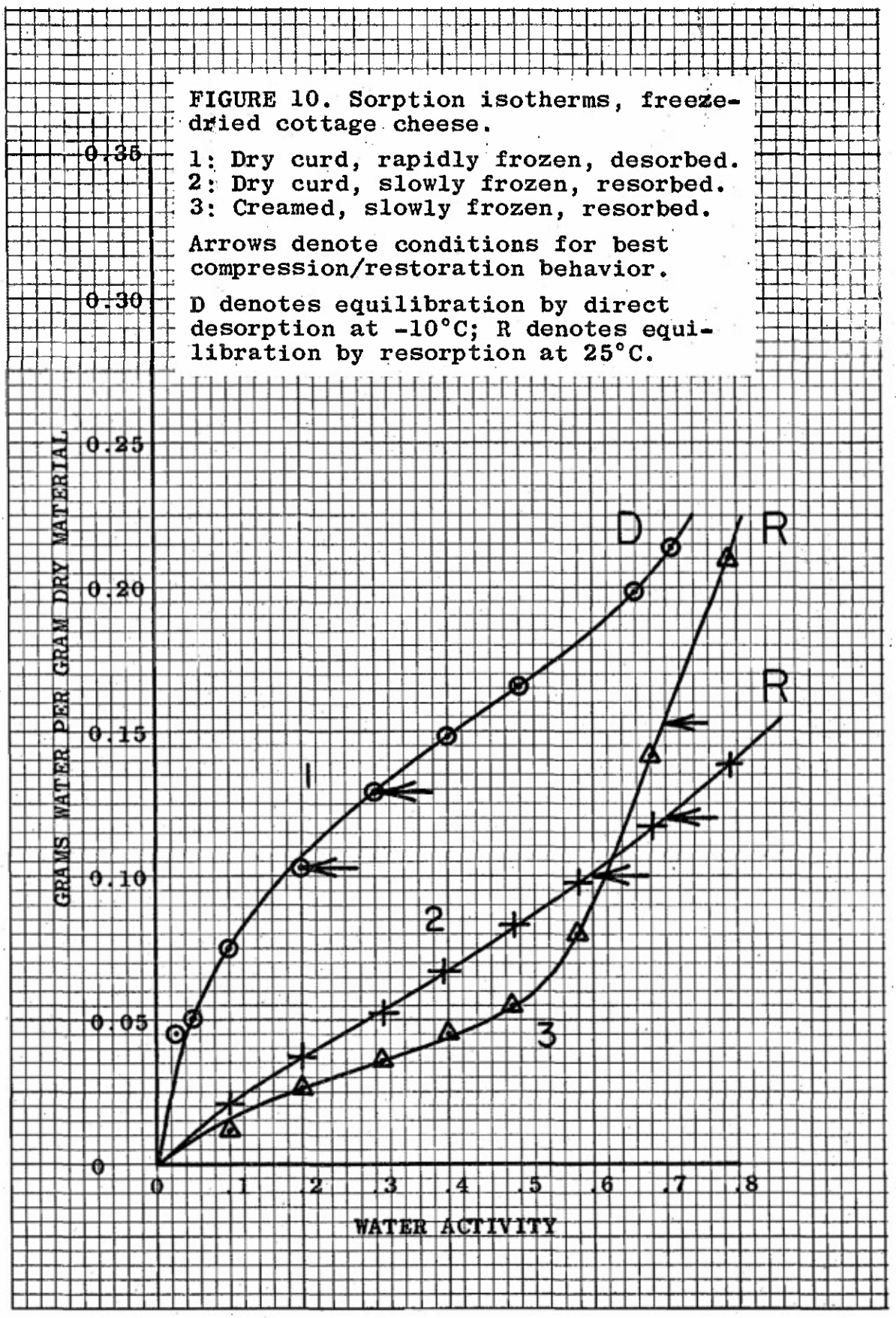


FIGURE 10. Sorption isotherms, freeze-dried cottage cheese.

1: Dry curd, rapidly frozen, desorbed.
2: Dry curd, slowly frozen, resorbed.
3: Creamed, slowly frozen, resorbed.

Arrows denote conditions for best compression/restoration behavior.

D denotes equilibration by direct desorption at -10°C; R denotes equilibration by resorption at 25°C.



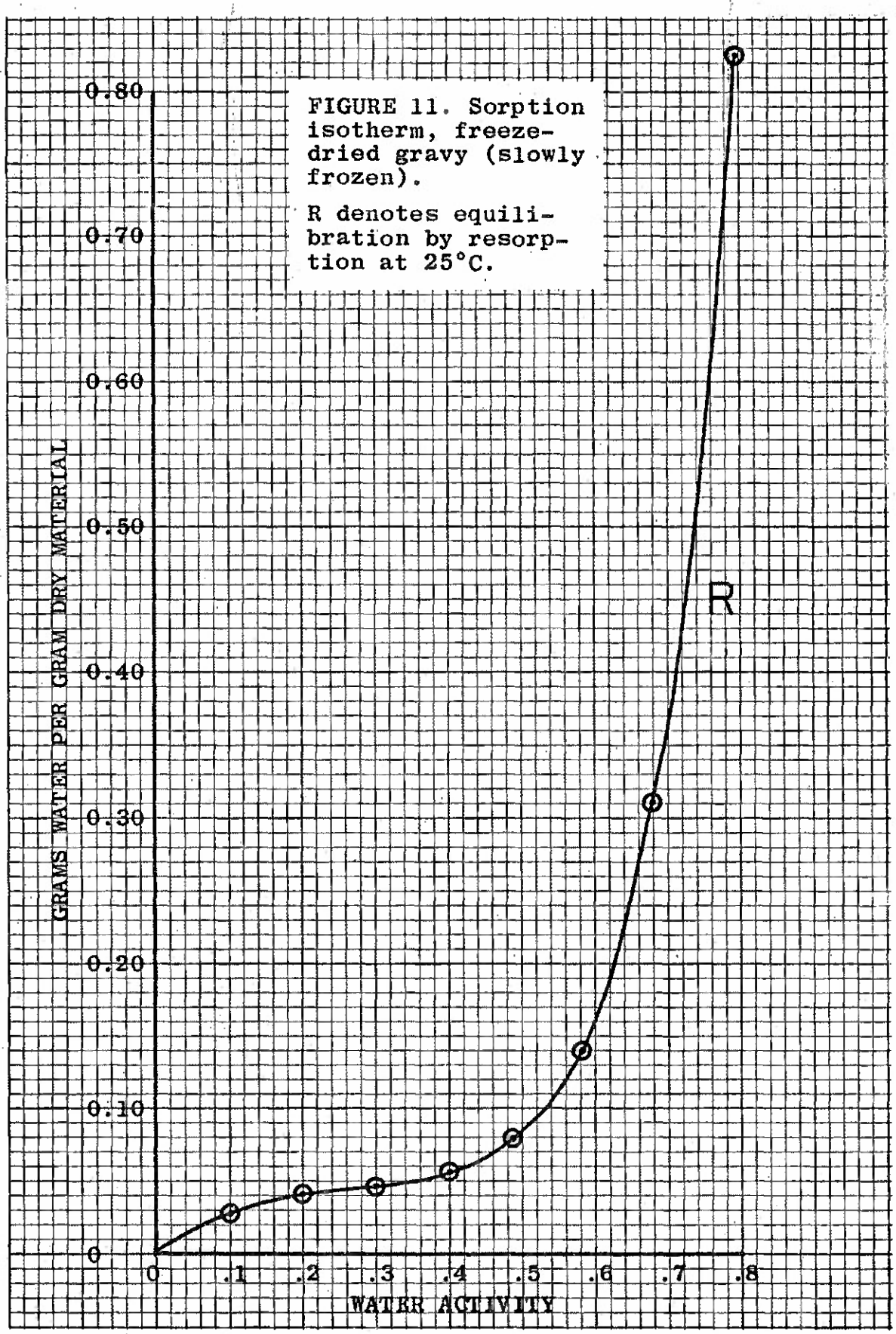


FIGURE 11. Sorption isotherm, freeze-dried gravy (slowly frozen).

R denotes equilibration by resorption at 25°C.

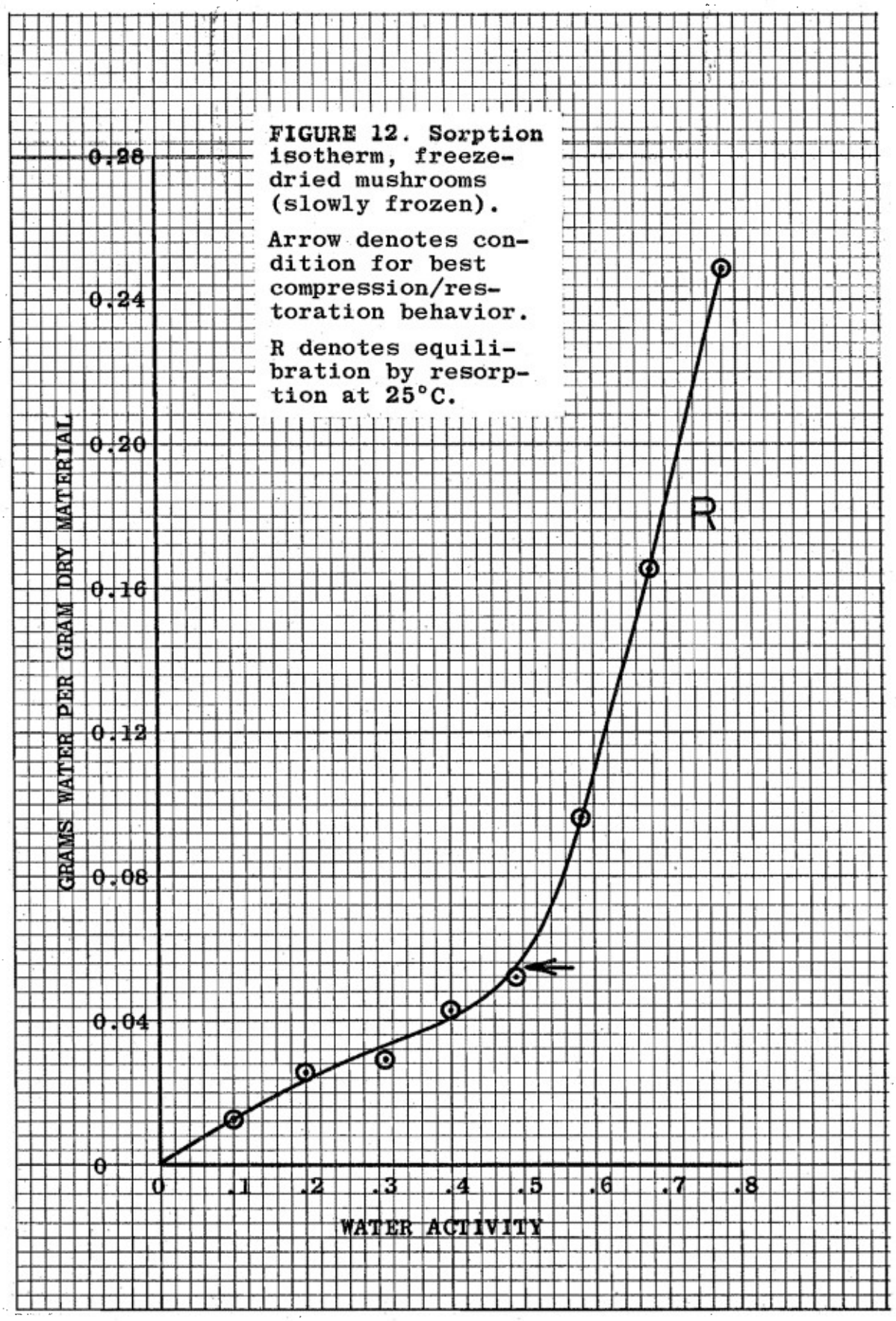


FIGURE 12. Sorption isotherm, freeze-dried mushrooms (slowly frozen).

Arrow denotes condition for best compression/restoration behavior.

R denotes equilibration by resorption at 25°C.

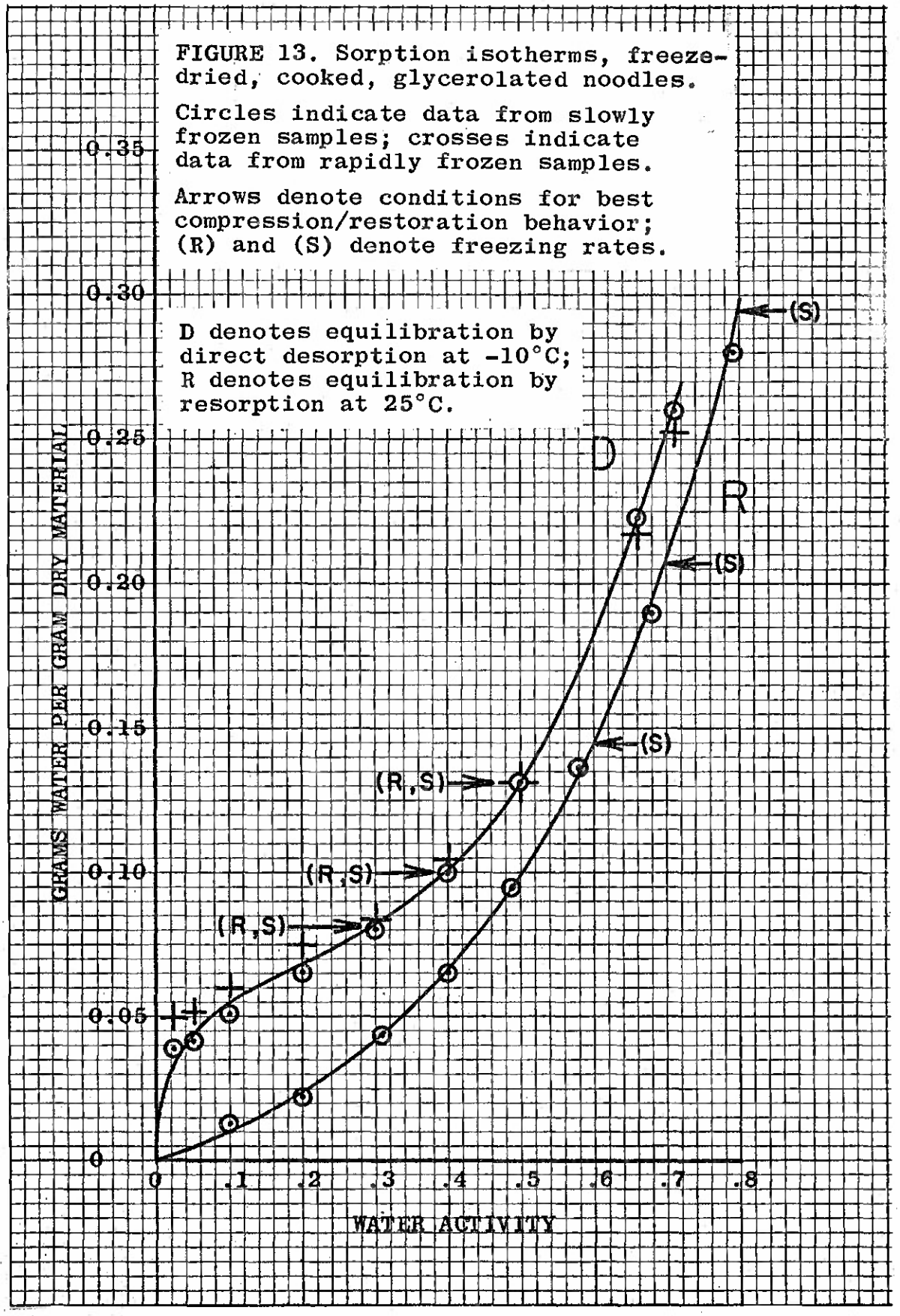


FIGURE 13. Sorption isotherms, freeze-dried, cooked, glycerolated noodles.

Circles indicate data from slowly frozen samples; crosses indicate data from rapidly frozen samples.

Arrows denote conditions for best compression/restoration behavior; (R) and (S) denote freezing rates.

D denotes equilibration by direct desorption at -10°C; R denotes equilibration by resorption at 25°C.

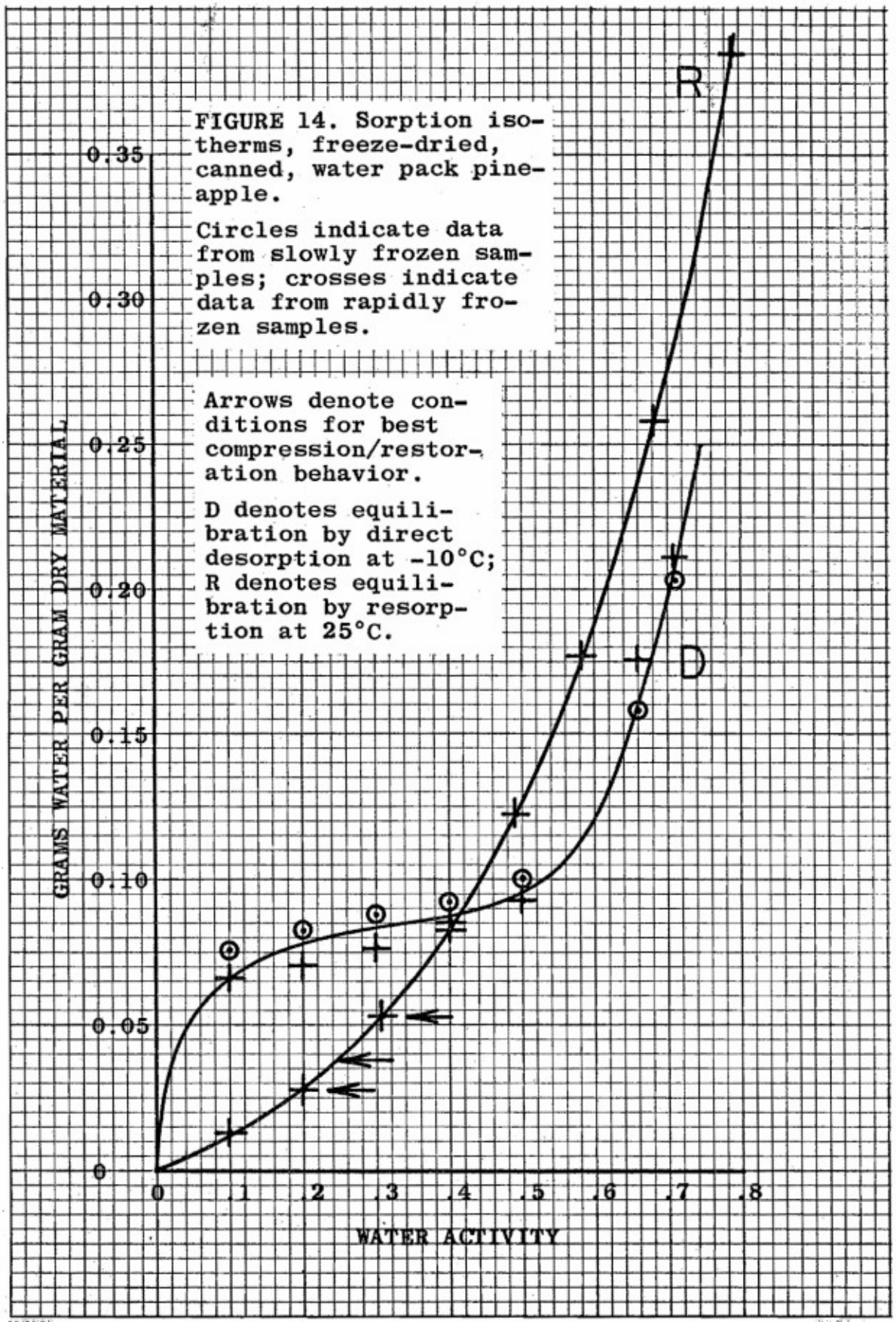


FIGURE 14. Sorption isotherms, freeze-dried, canned, water pack pineapple.
Circles indicate data from slowly frozen samples; crosses indicate data from rapidly frozen samples.
Arrows denote conditions for best compression/restoration behavior.
D denotes equilibration by direct desorption at -10°C; R denotes equilibration by resorption at 25°C.
R
D
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0
GRAMS WATER PER GRAM DRY MATERIAL
0
.1
.2
.3
.4
.5
.6
.7
.8
WATER ACTIVITY

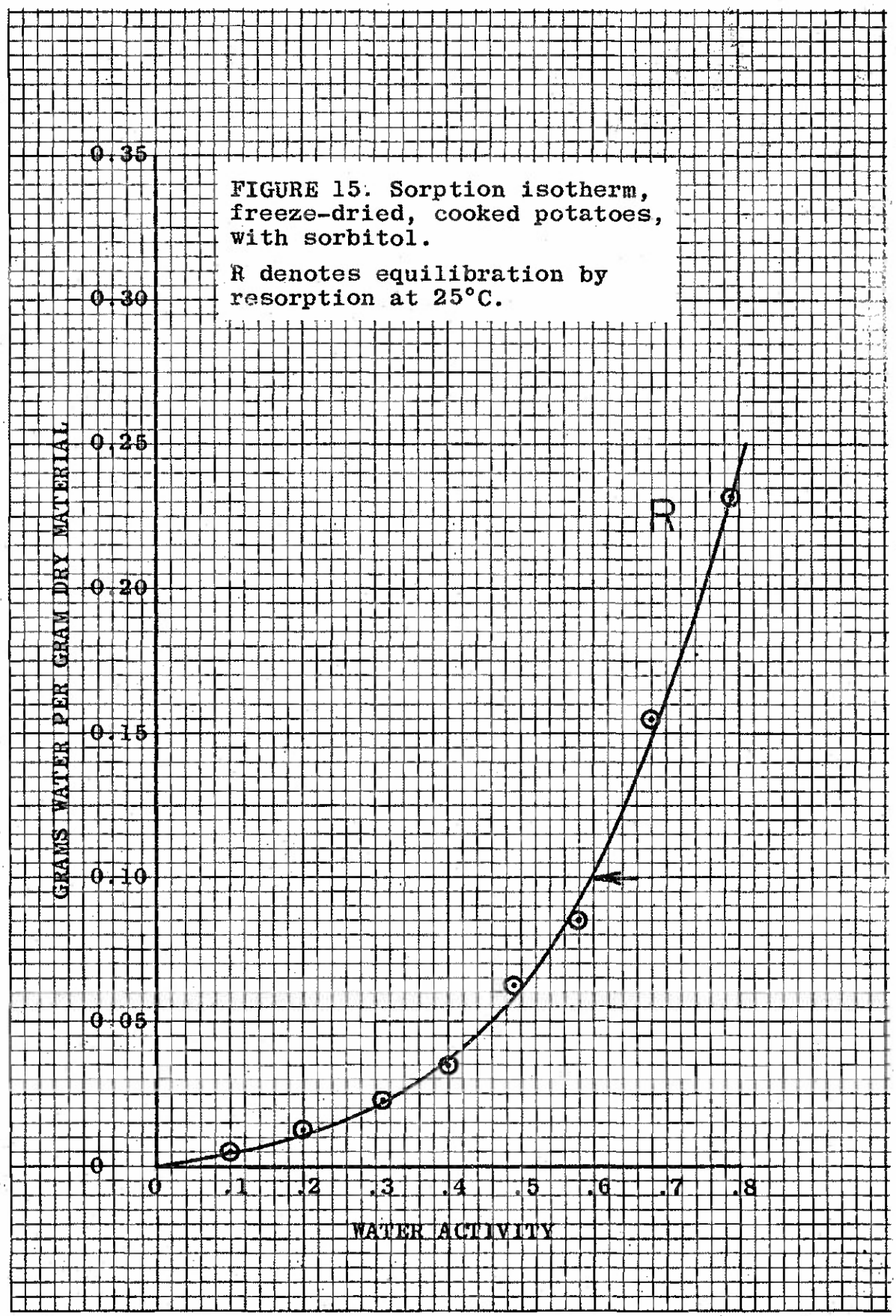


FIGURE 15. Sorption isotherm, freeze-dried, cooked potatoes, with sorbitol.

R denotes equilibration by resorption at 25°C.

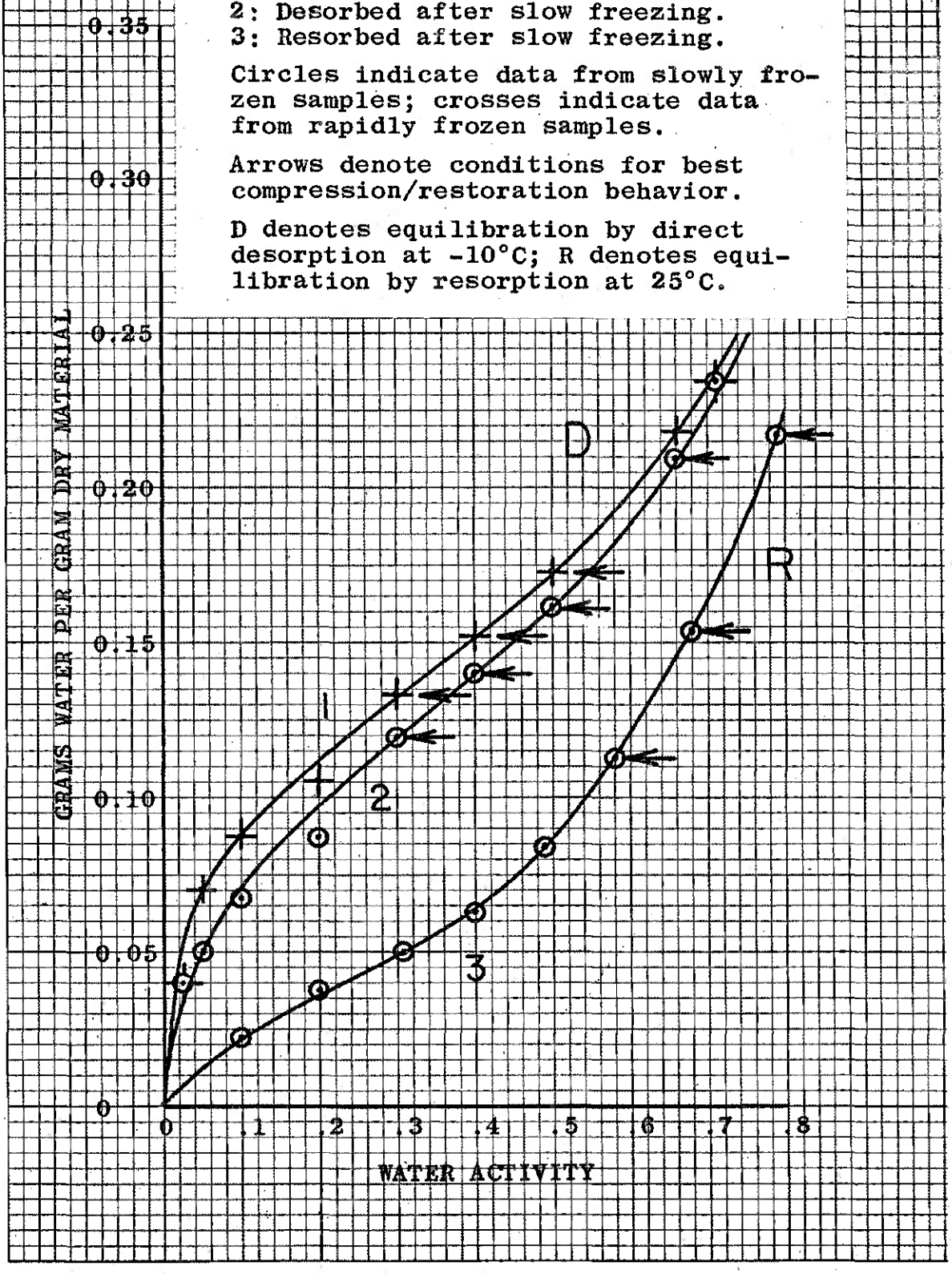
FIGURE 16. Sorption isotherms, freeze-dried, canned, water pack tuna.

1: Desorbed after rapid freezing.
2: Desorbed after slow freezing.
3: Resorbed after slow freezing.

Circles indicate data from slowly frozen samples; crosses indicate data from rapidly frozen samples.

Arrows denote conditions for best compression/restoration behavior.

D denotes equilibration by direct desorption at -10°C; R denotes equilibration by resorption at 25°C.



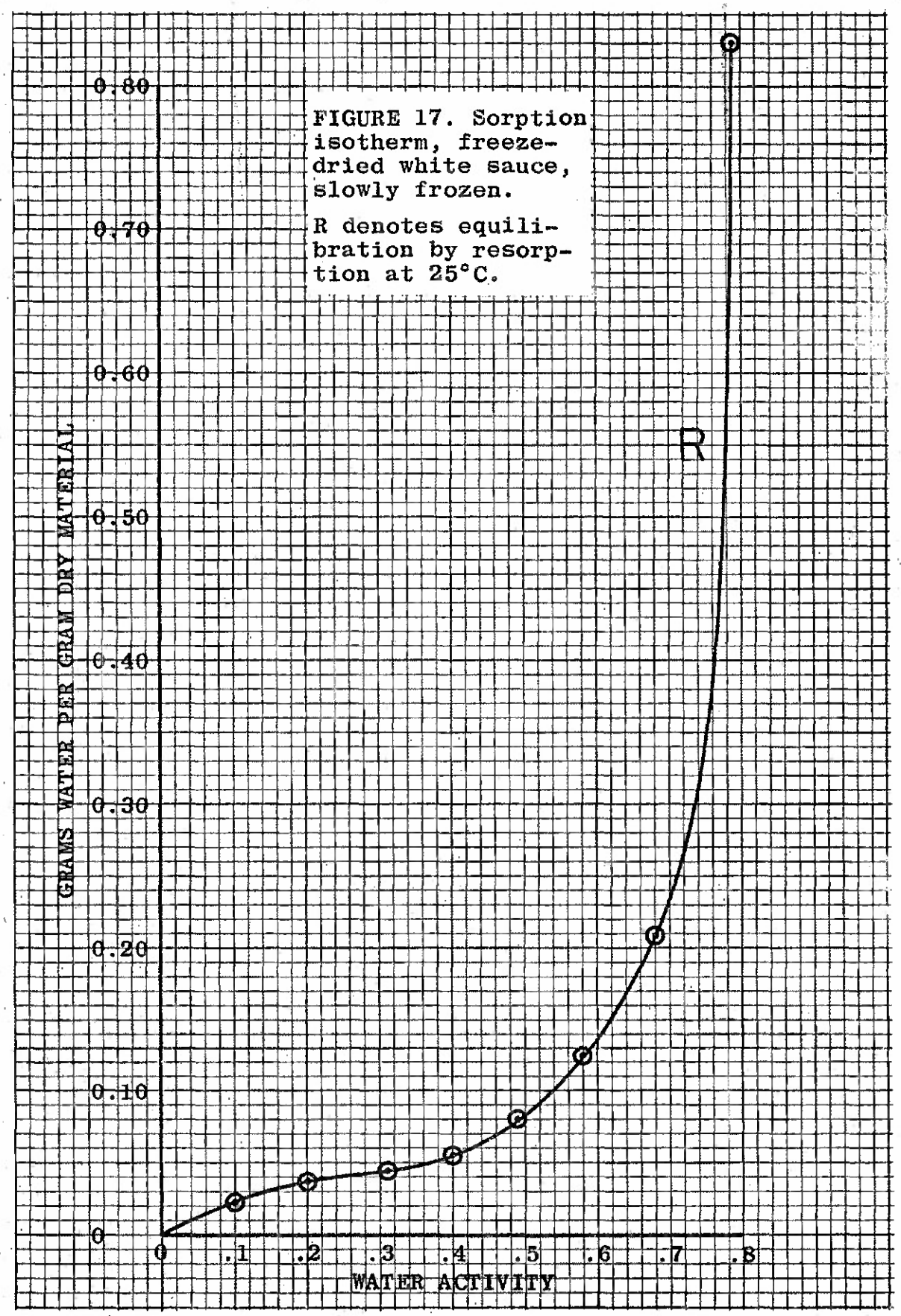


FIGURE 17. Sorption isotherm, freeze-dried white sauce, slowly frozen.

R denotes equilibration by resorption at 25°C.

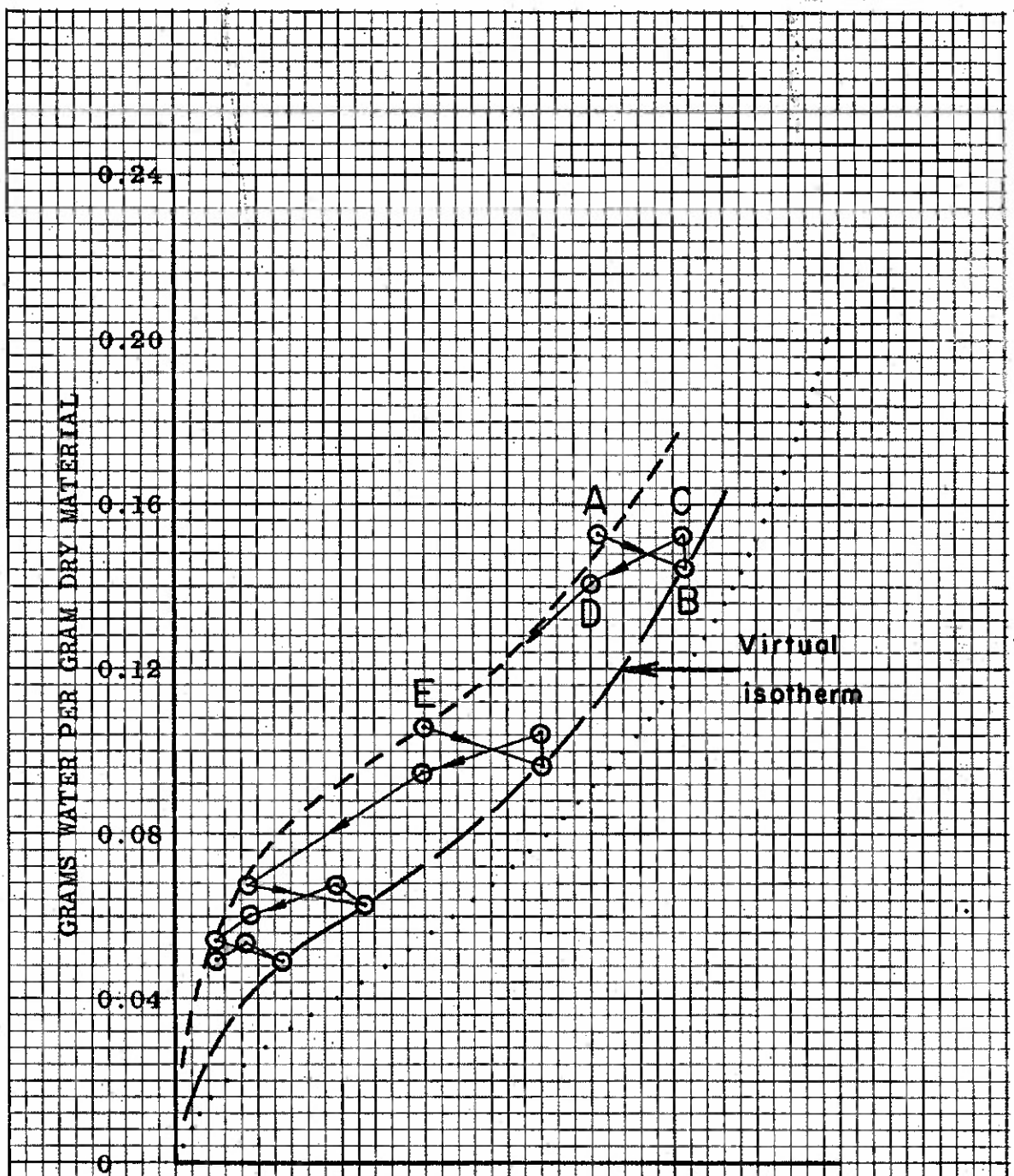


FIGURE 18. "Virtual sorption isotherm" obtained from freeze-dried beef, slowly frozen. See pp.30-31 for explanation.

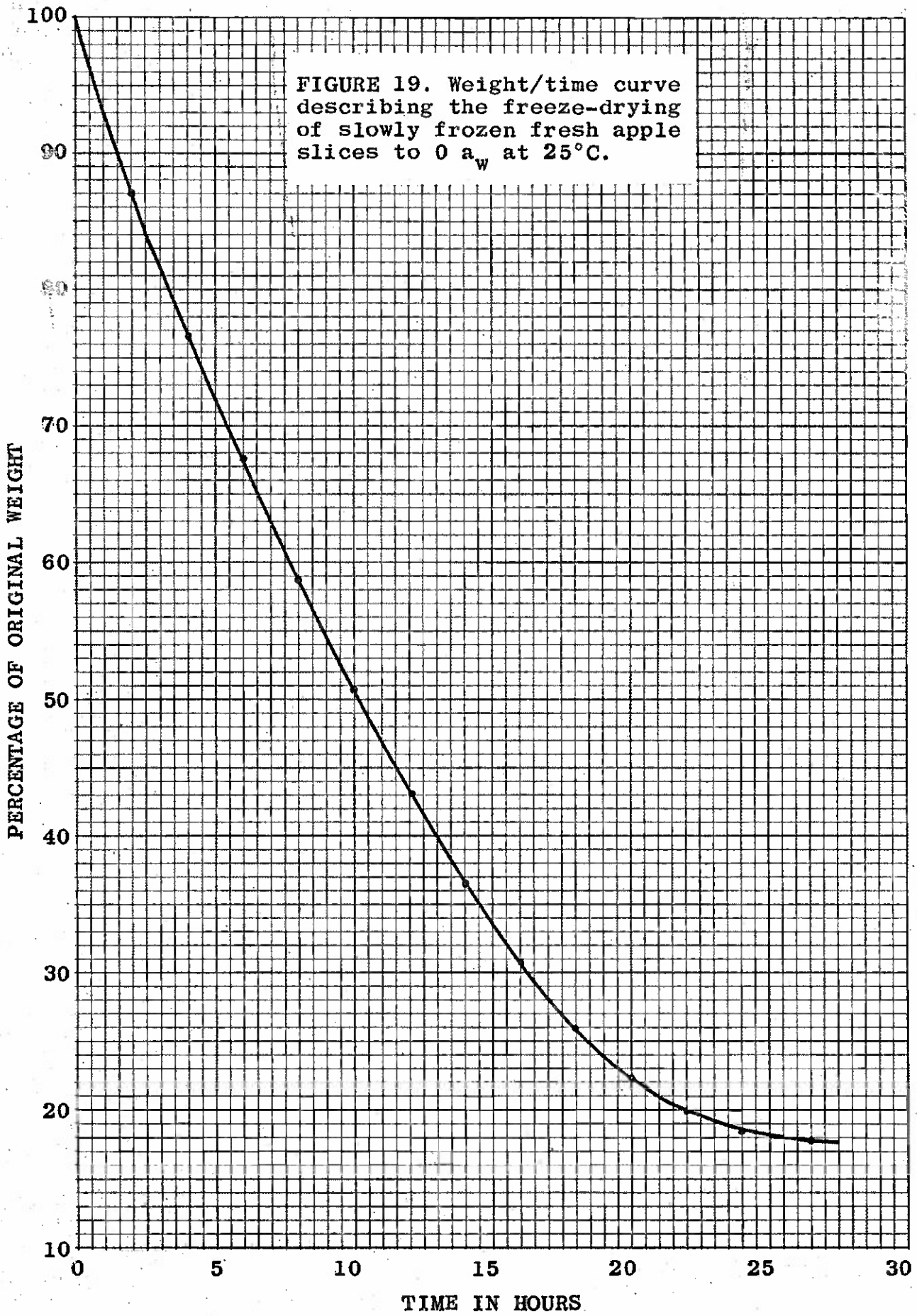


FIGURE 19. Weight/time curve describing the freeze-drying of slowly frozen fresh apple slices to 0 a_w at 25°C.

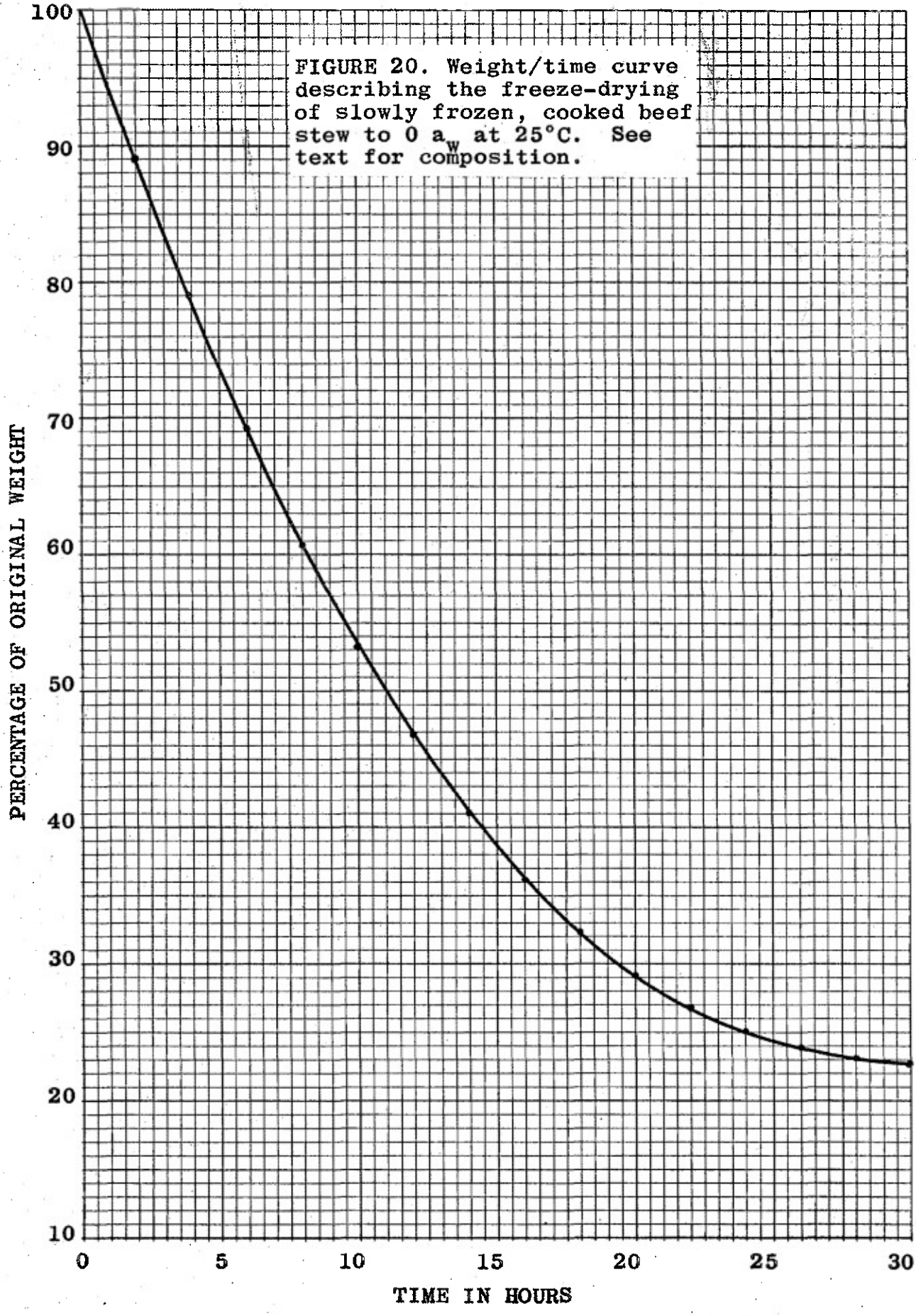


FIGURE 20. Weight/time curve describing the freeze-drying of slowly frozen, cooked beef stew to 0 a_w at 25°C. See text for composition.

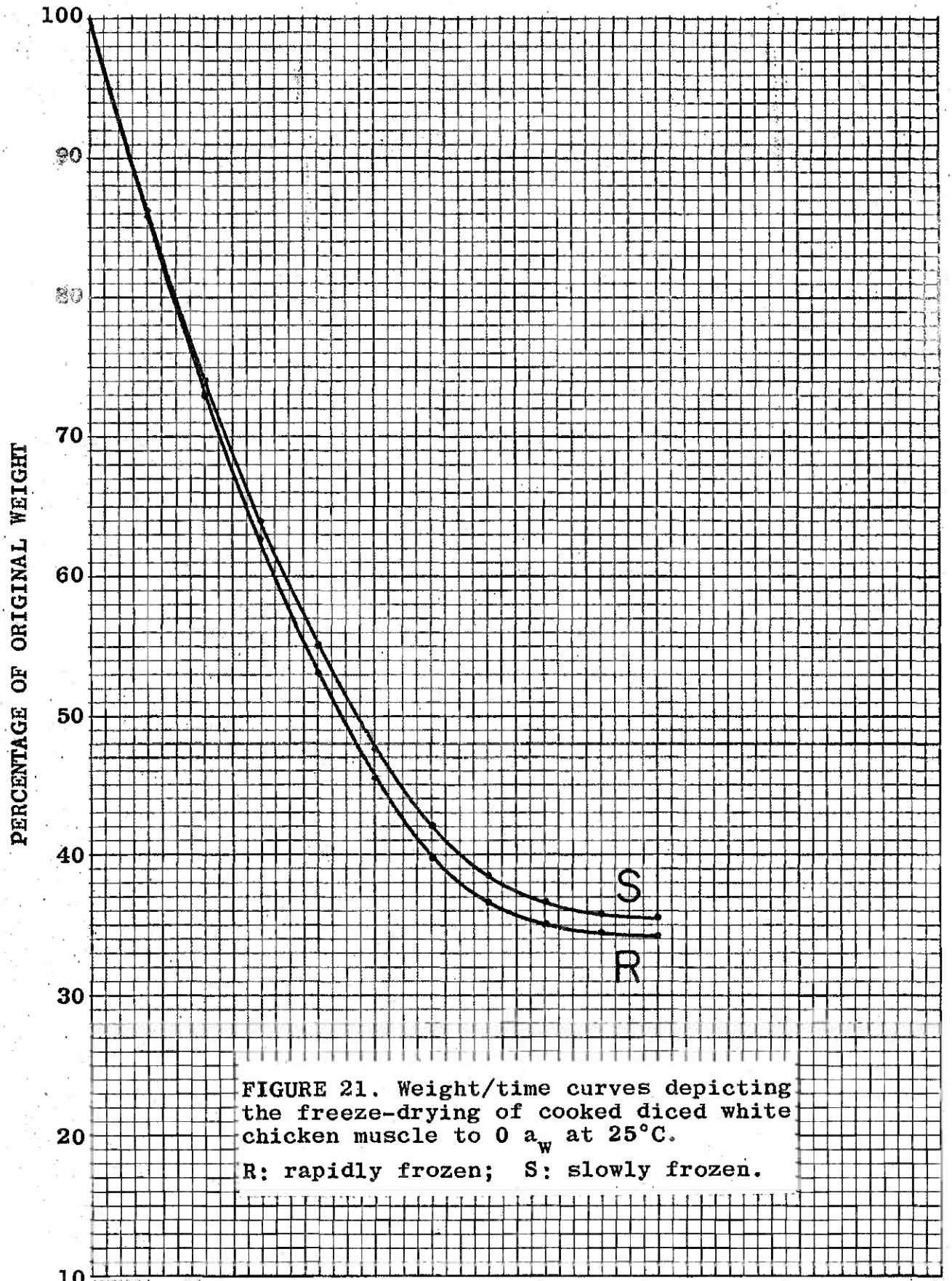


FIGURE 21. Weight/time curves depicting the freeze-drying of cooked diced white chicken muscle to 0 a_w at 25°C.

R: rapidly frozen; S: slowly frozen.

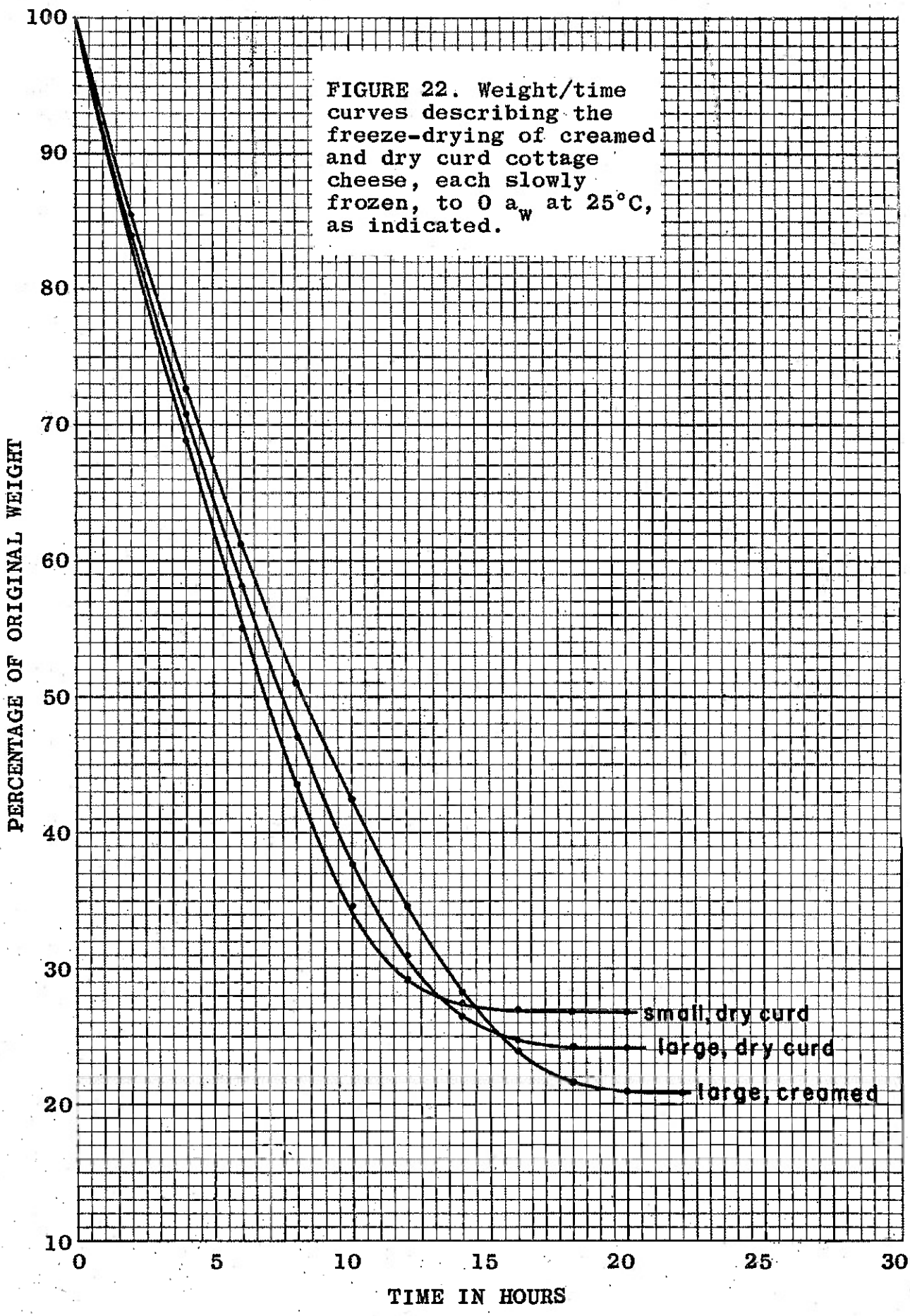


FIGURE 22. Weight/time curves describing the freeze-drying of creamed and dry curd cottage cheese, each slowly frozen, to 0 a_w at 25°C, as indicated.

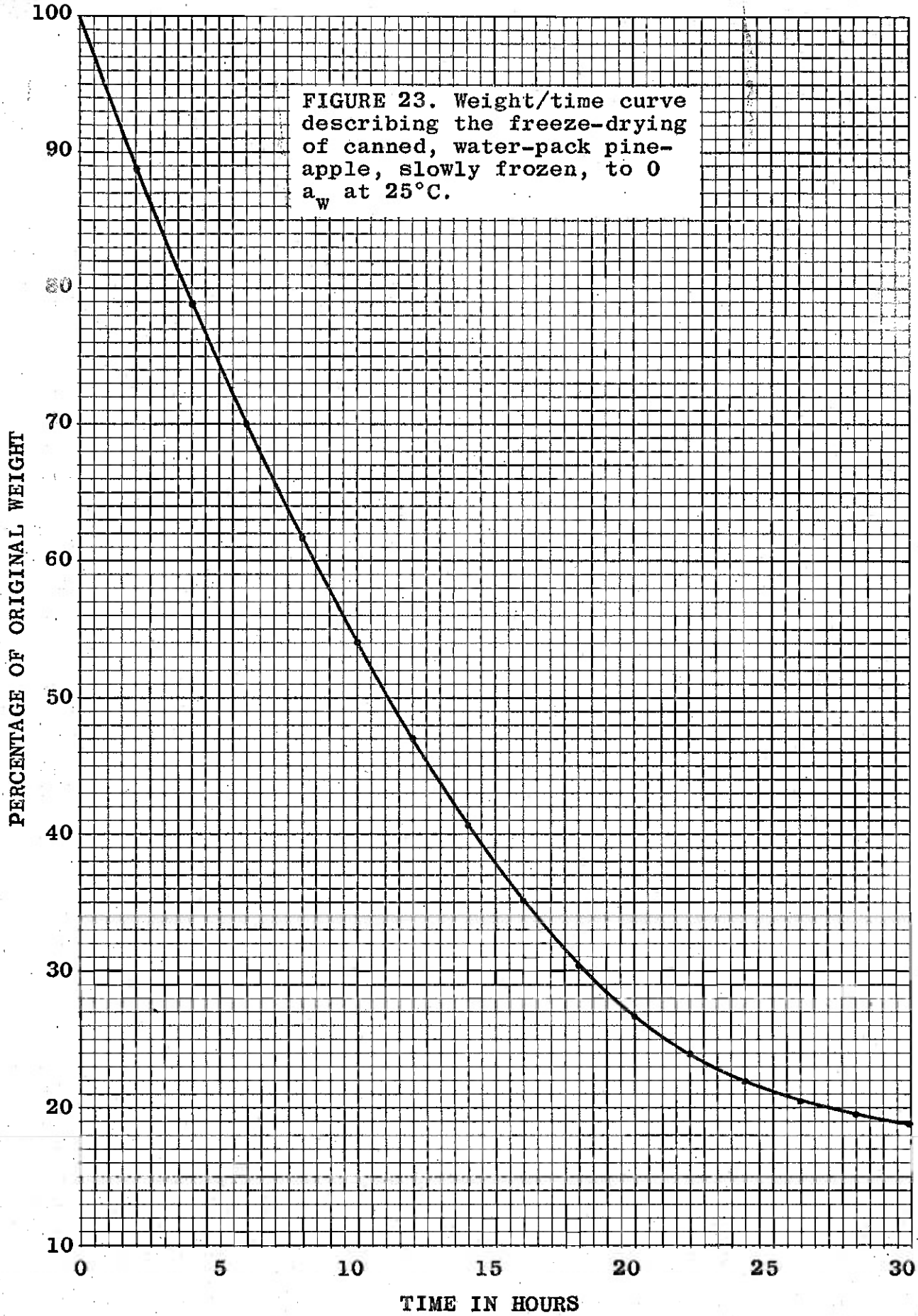


FIGURE 23. Weight/time curve describing the freeze-drying of canned, water-pack pineapple, slowly frozen, to 0 a_w at 25°C.

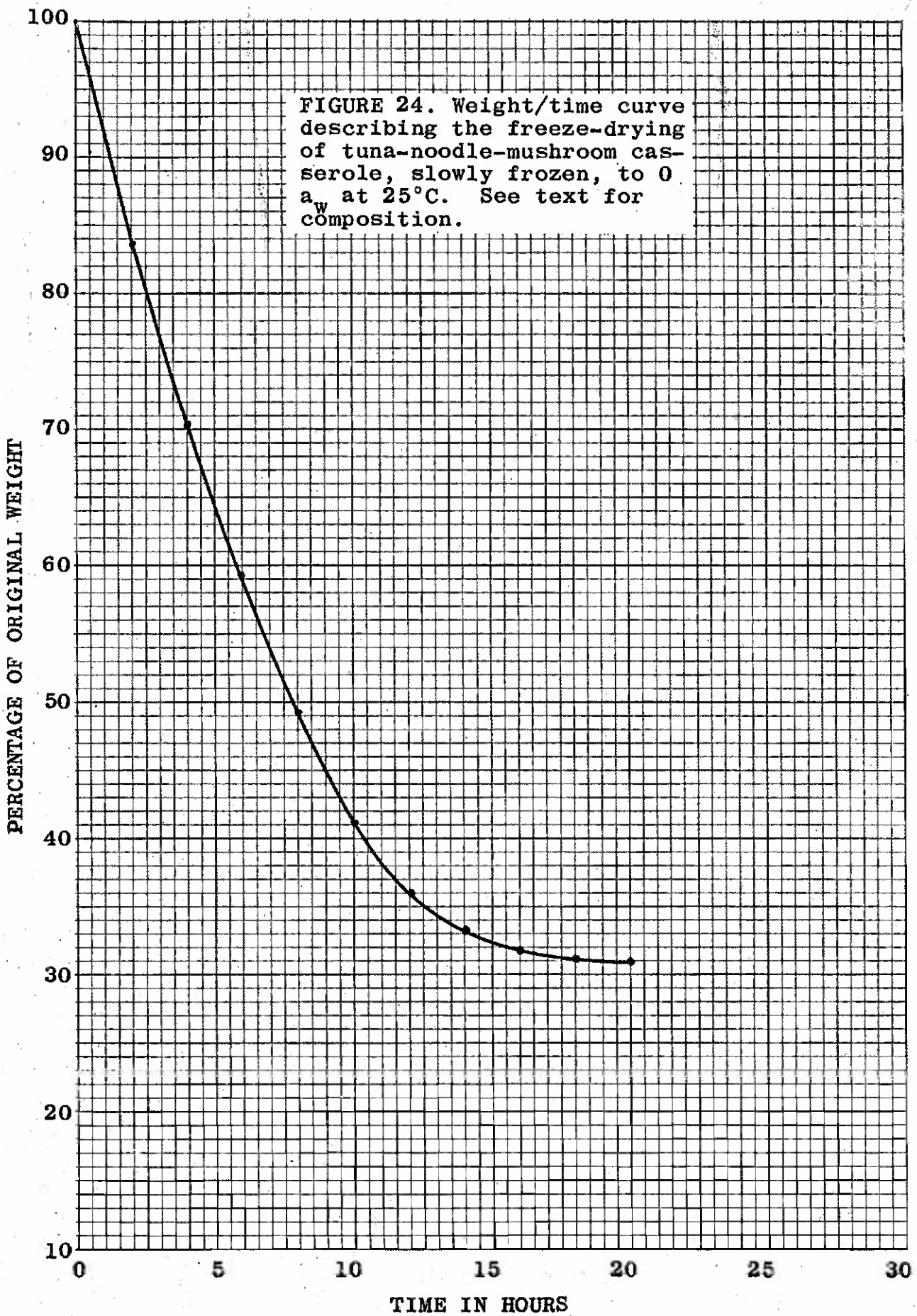


FIGURE 24. Weight/time curve describing the freeze-drying of tuna-noodle-mushroom casserole, slowly frozen, to 0 a_w at 25°C. See text for composition.

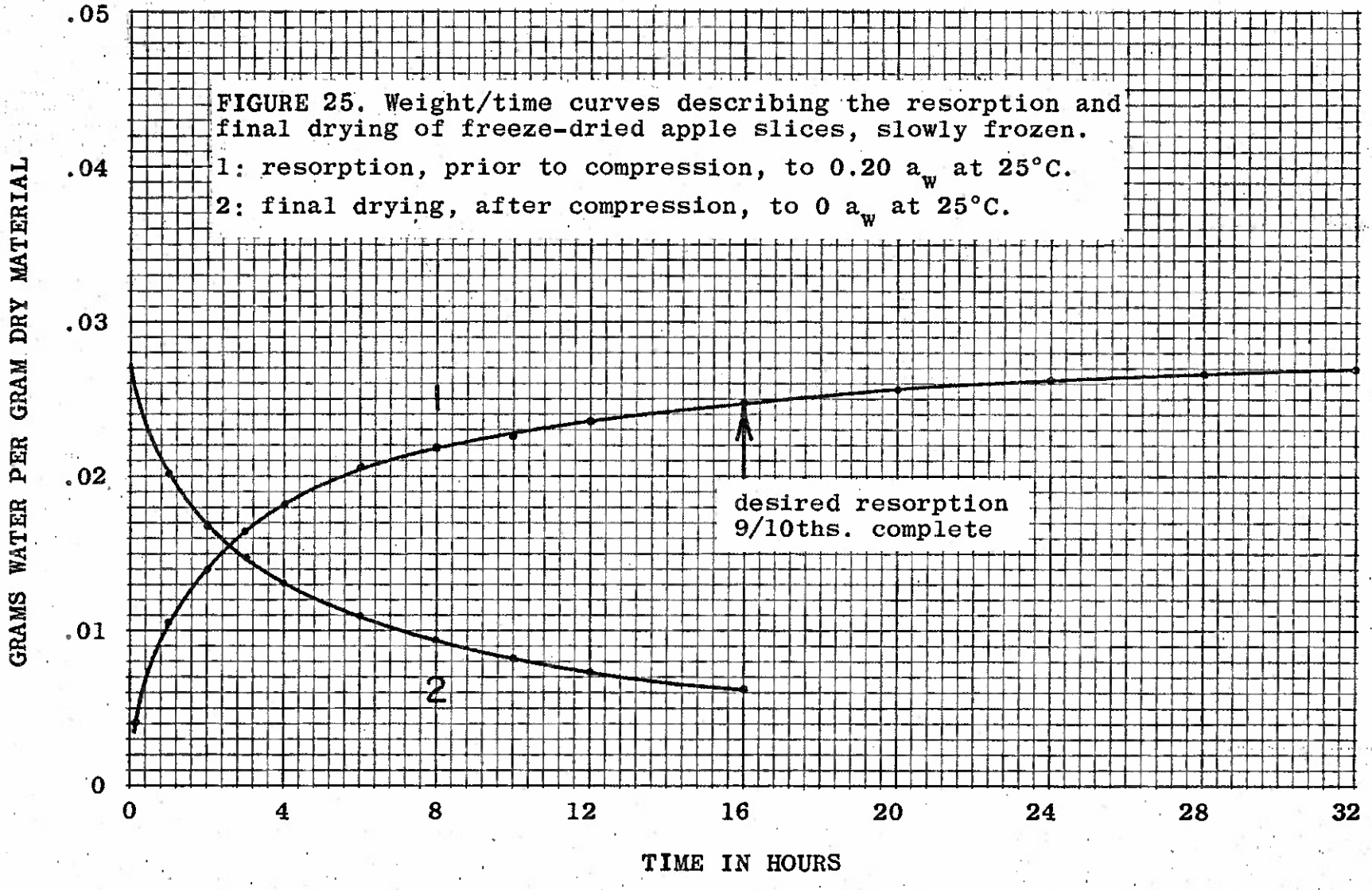


FIGURE 25. Weight/time curves describing the resorption and final drying of freeze-dried apple slices, slowly frozen.
1: resorption, prior to compression, to 0.20 a_w at 25°C.
2: final drying, after compression, to 0 a_w at 25°C.

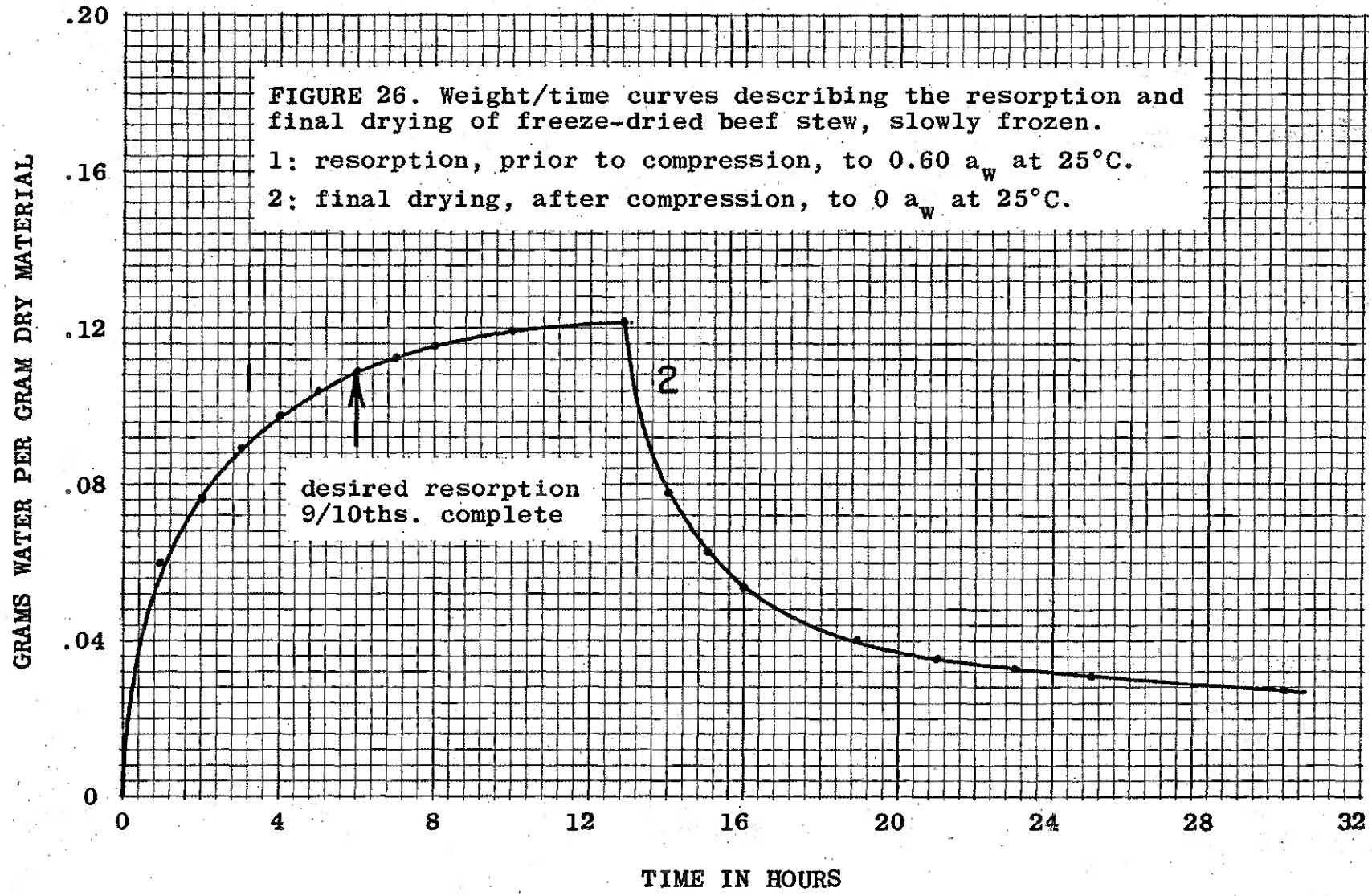


FIGURE 26. Weight/time curves describing the resorption and final drying of freeze-dried beef stew, slowly frozen.

1: resorption, prior to compression, to 0.60 a_w at 25°C.

2: final drying, after compression, to 0 a_w at 25°C.

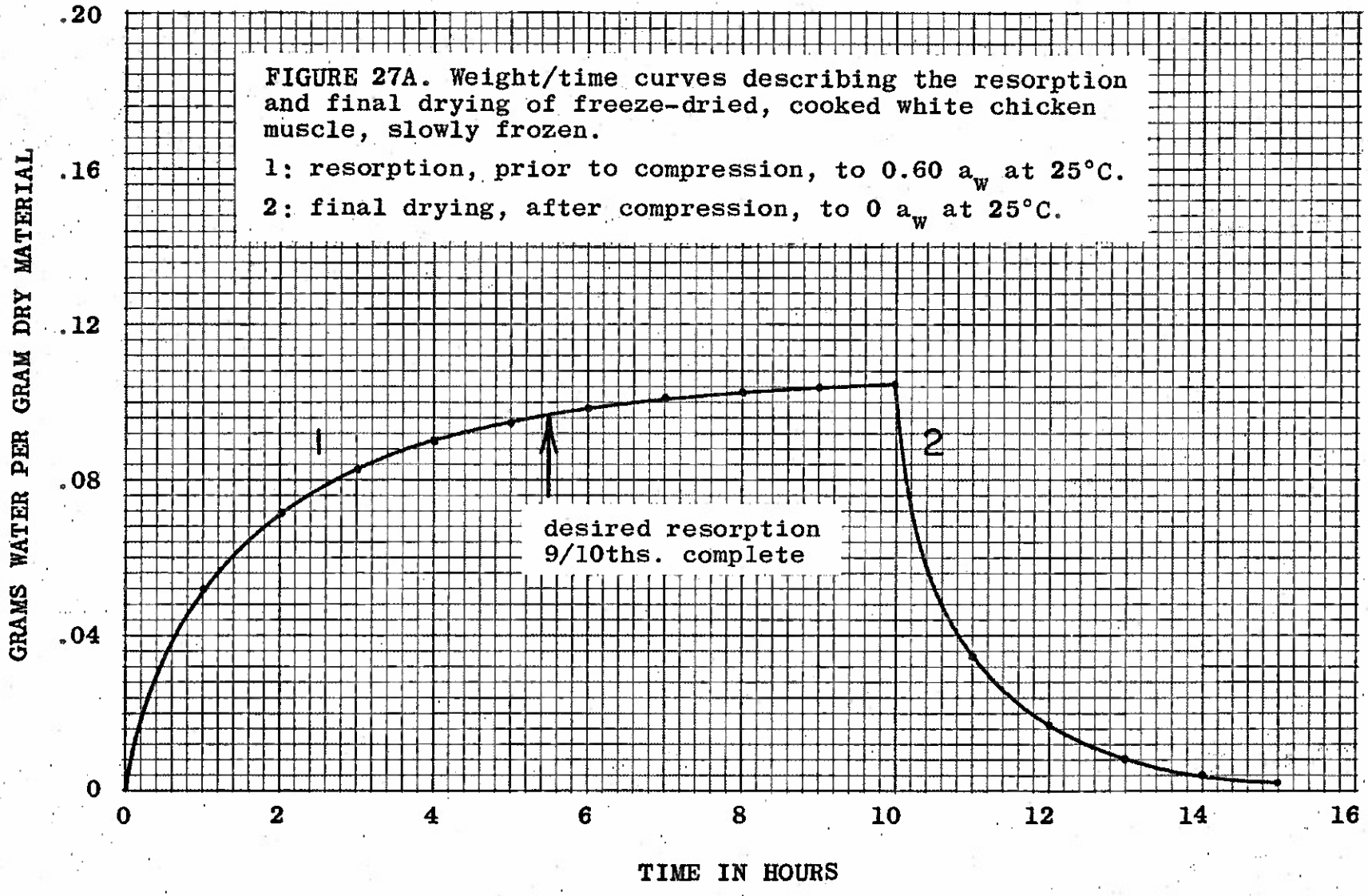


FIGURE 27A. Weight/time curves describing the resorption and final drying of freeze-dried, cooked white chicken muscle, slowly frozen.
1: resorption, prior to compression, to 0.60 a_w at 25°C.
2: final drying, after compression, to 0 a_w at 25°C.
GRAMS WATER PER GRAM DRY MATERIAL
.20
.16
.12
.08
.04
0
0
2
4
6
8
10
12
14
16
TIME IN HOURS
1
2
desired resorption
9/10ths. complete

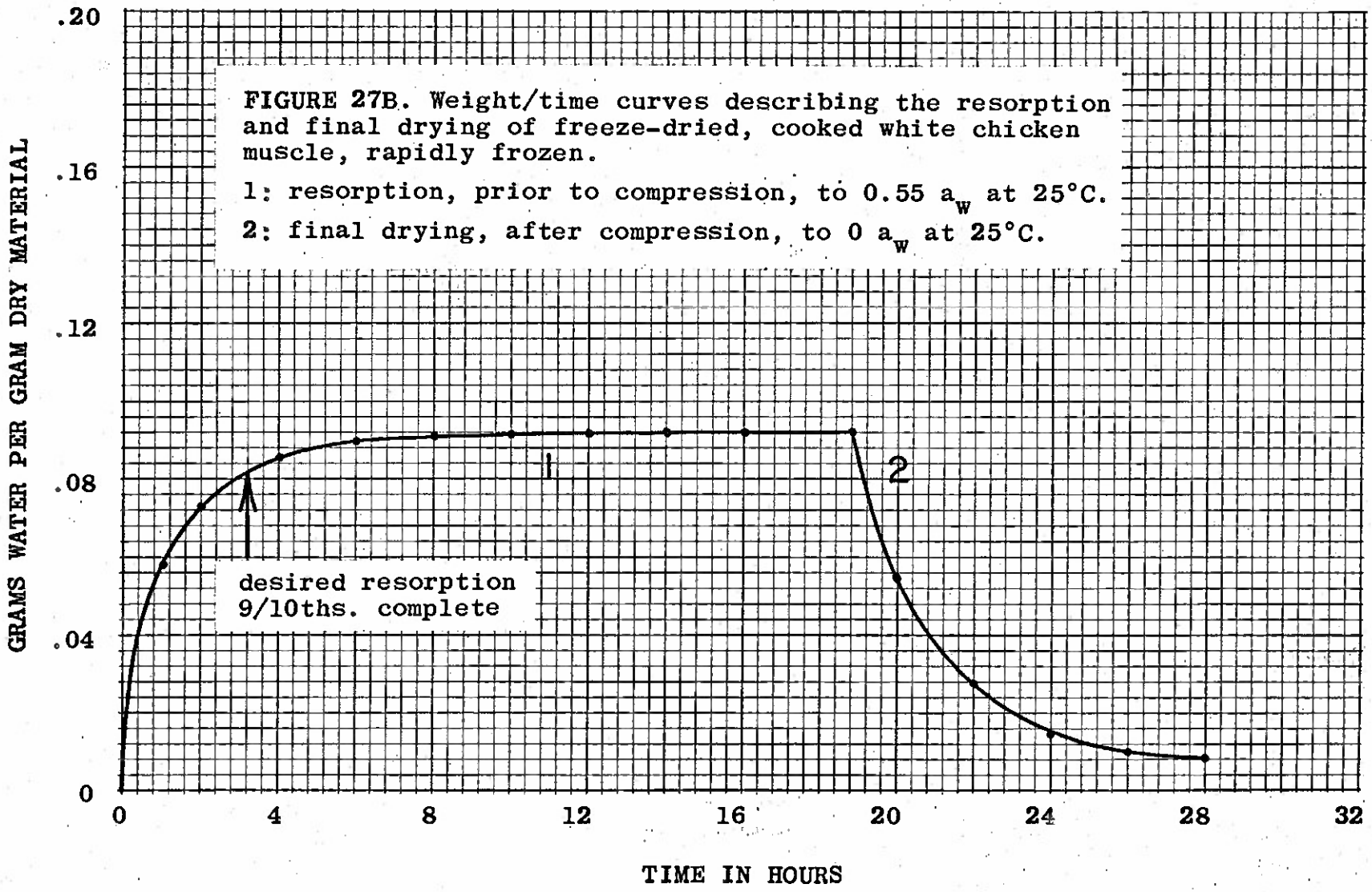


FIGURE 27B. Weight/time curves describing the resorption and final drying of freeze-dried, cooked white chicken muscle, rapidly frozen.

1: resorption, prior to compression, to 0.55 a_w at 25°C.

2: final drying, after compression, to 0 a_w at 25°C.

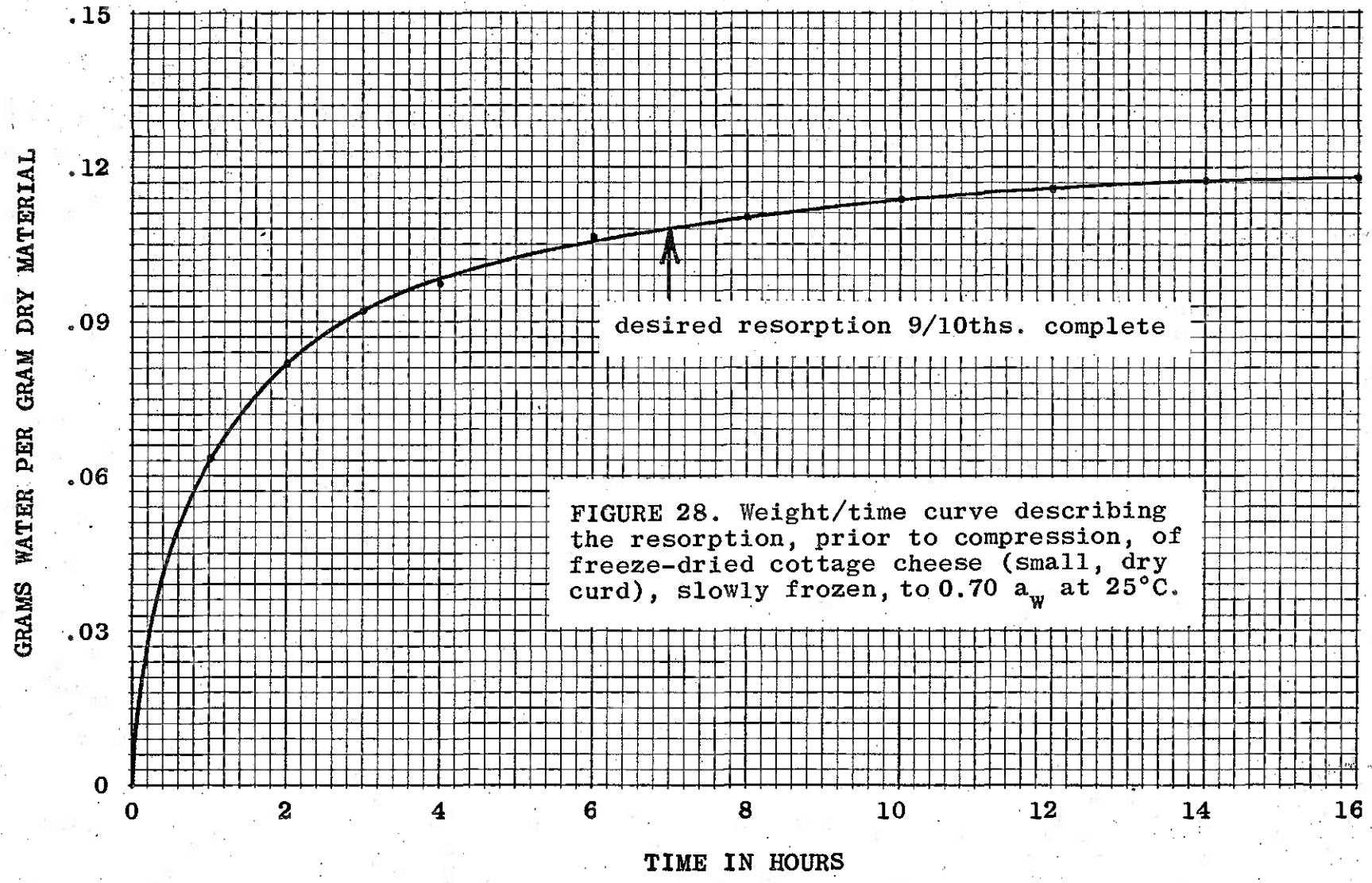


FIGURE 28. Weight/time curve describing the resorption, prior to compression, of freeze-dried cottage cheese (small, dry curd), slowly frozen, to 0.70 a_w at 25°C.

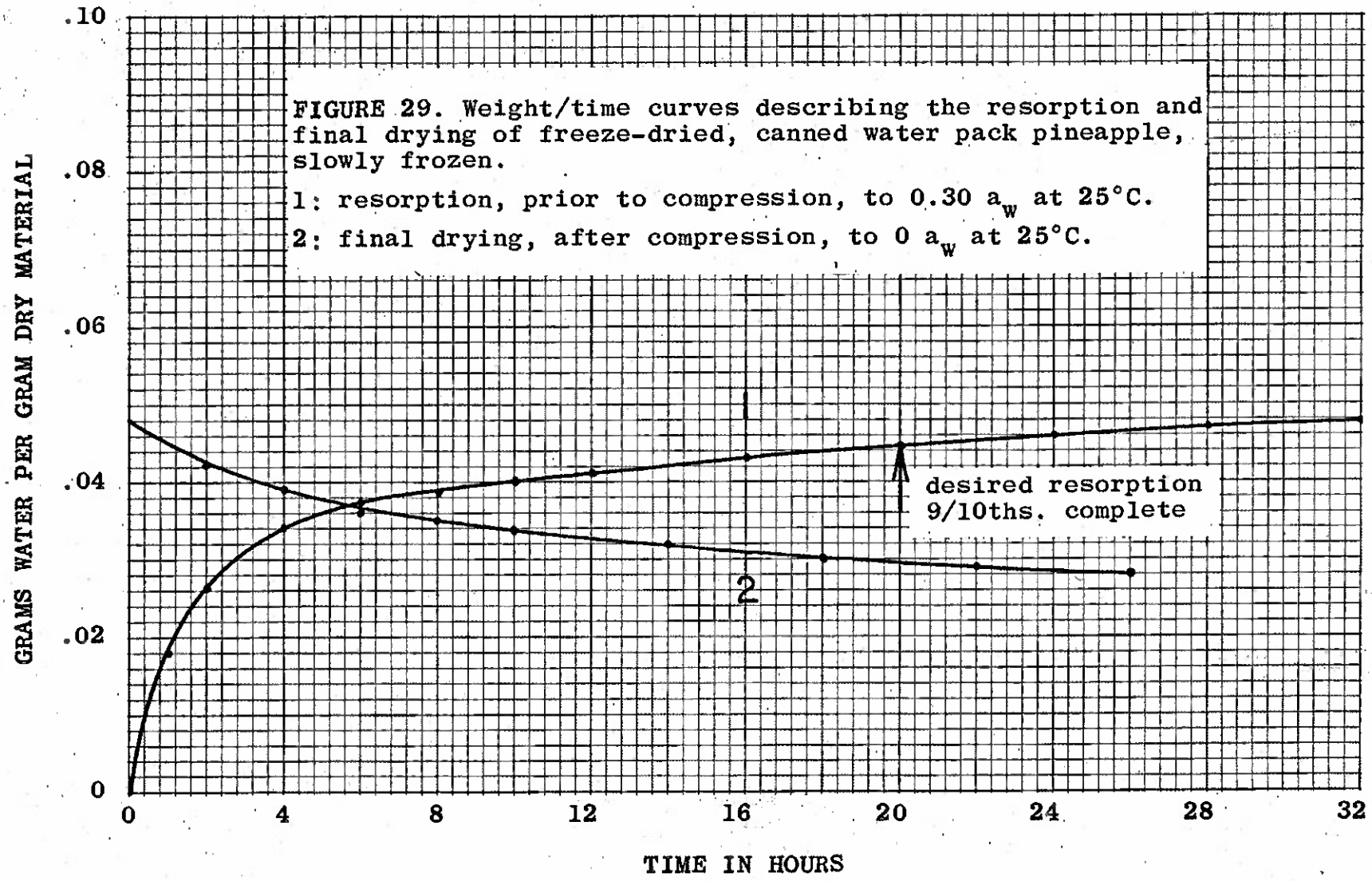


FIGURE 29. Weight/time curves describing the resorption and final drying of freeze-dried, canned water pack pineapple, slowly frozen.

1: resorption, prior to compression, to 0.30 a_w at 25°C.

2: final drying, after compression, to 0 a_w at 25°C.

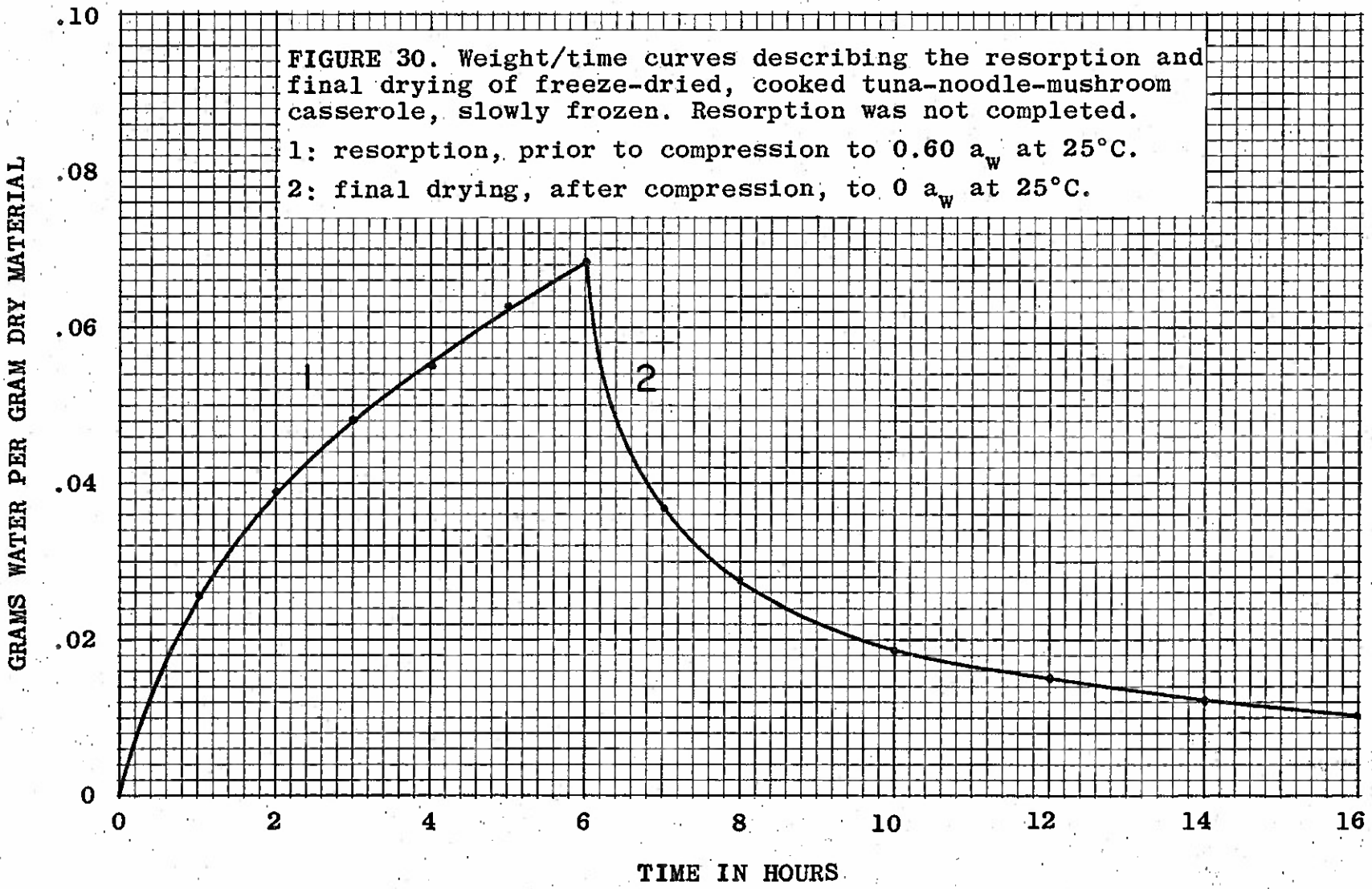


FIGURE 30. Weight/time curves describing the resorption and final drying of freeze-dried, cooked tuna-noodle-mushroom casserole, slowly frozen. Resorption was not completed.

1: resorption, prior to compression to 0.60 a_w at 25°C.

2: final drying, after compression, to 0 a_w at 25°C.

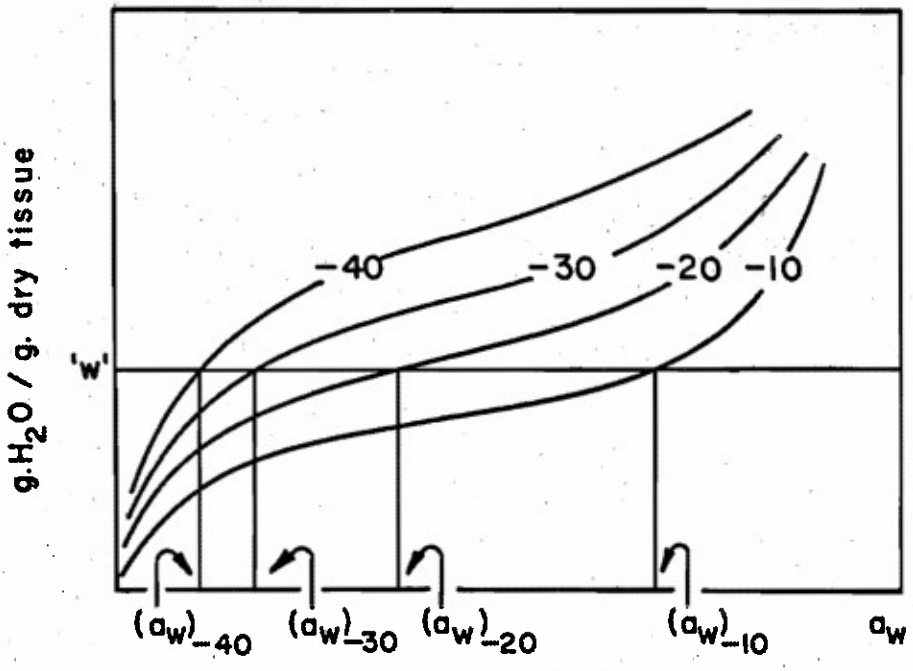


FIGURE 31. Extents to which a_w must be reduced to effect desorption to same water content at different freeze-drying temperatures (drawing not to scale).

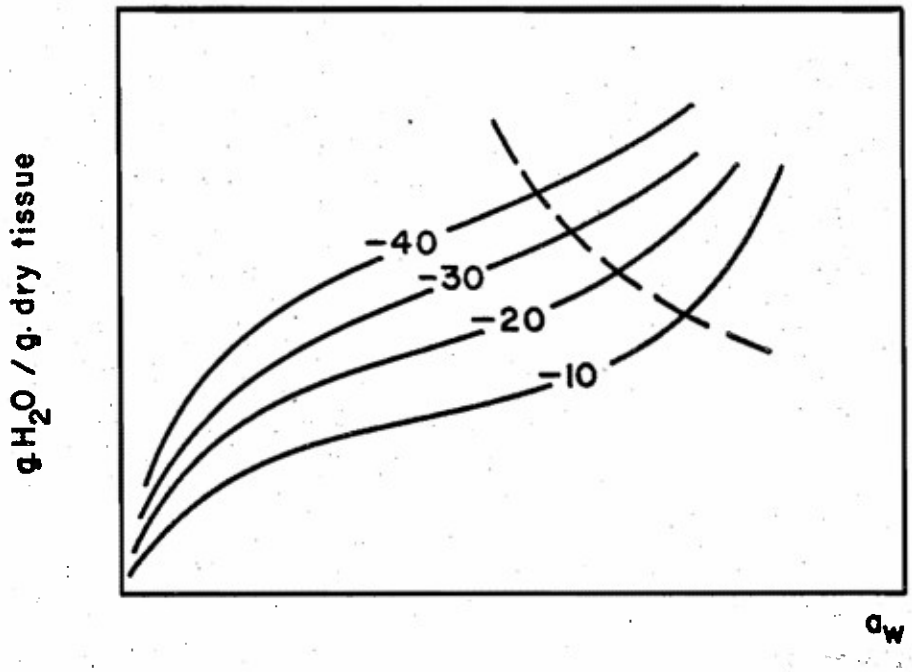


FIGURE 32. Extents to which material must be desorbed for best compression at the freeze-drying temperature (not to scale).

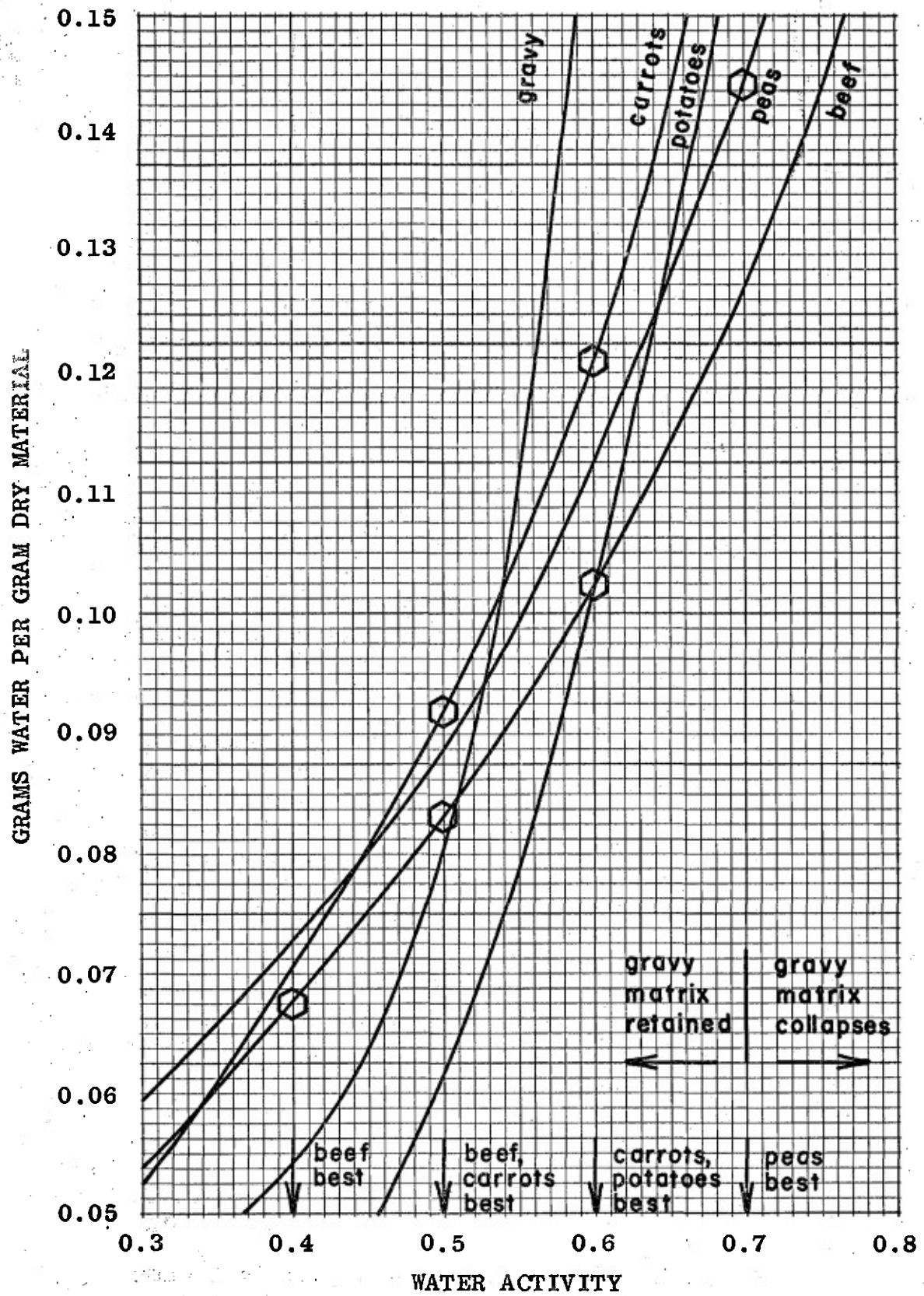


FIGURE 33. Resorption isotherms characteristic of components of beef stew (see text). Hexagonal markers denote best compression/restoration behavior.

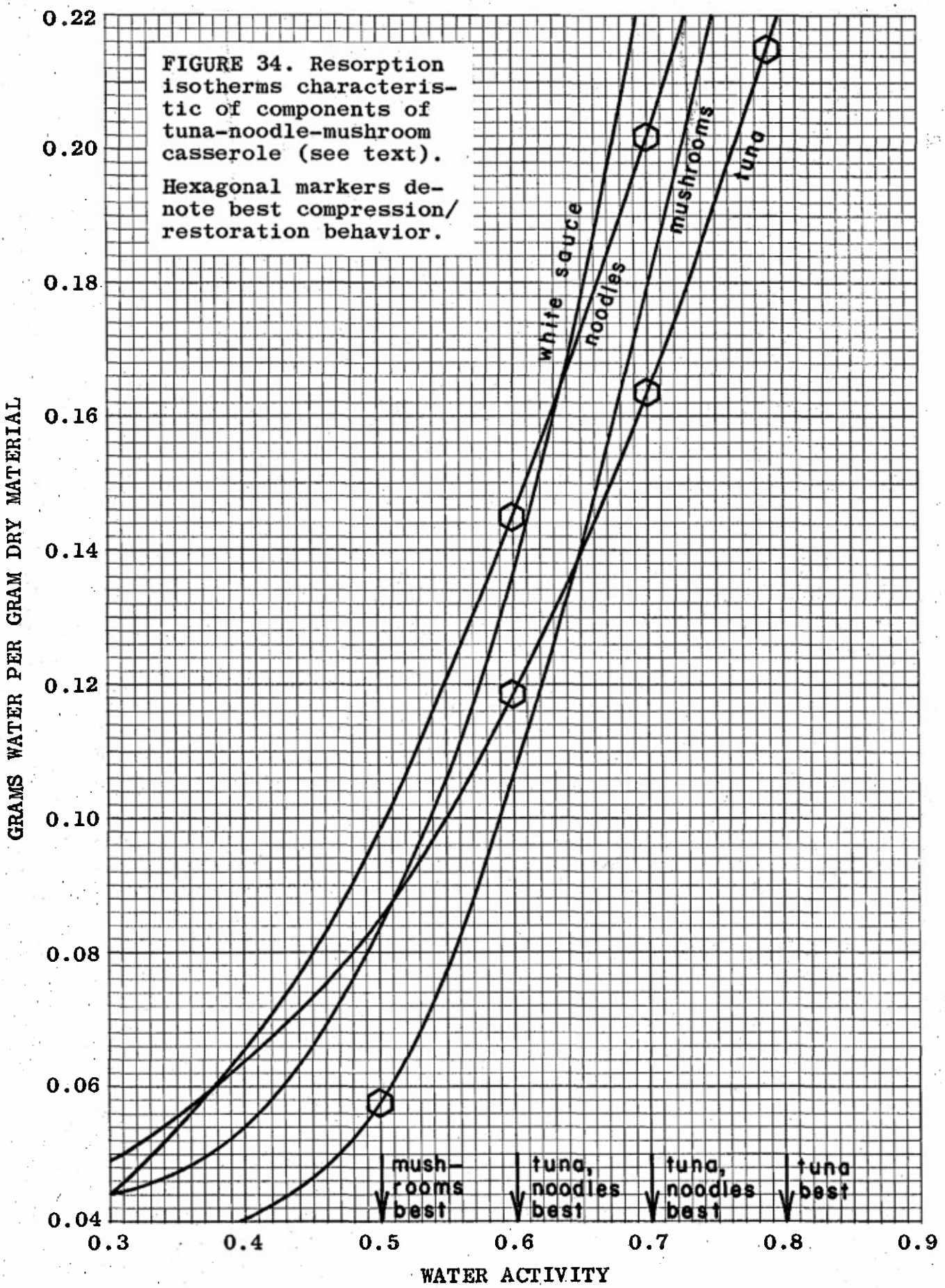


FIGURE 34. Resorption isotherms characteristic of components of tuna-noodle-mushroom casserole (see text).
Hexagonal markers denote best compression/restoration behavior.
white sauce
noodles
mushrooms
tuna
mush-rooms best
tuna, noodles best
tuna, noodles best
tuna best
GRAMS WATER PER GRAM DRY MATERIAL
0.22
0.20
0.18
0.16
0.14
0.12
0.10
0.08
0.06
0.04
0.3
0.4
0.5
0.6
0.7
0.8
0.9
WATER ACTIVITY

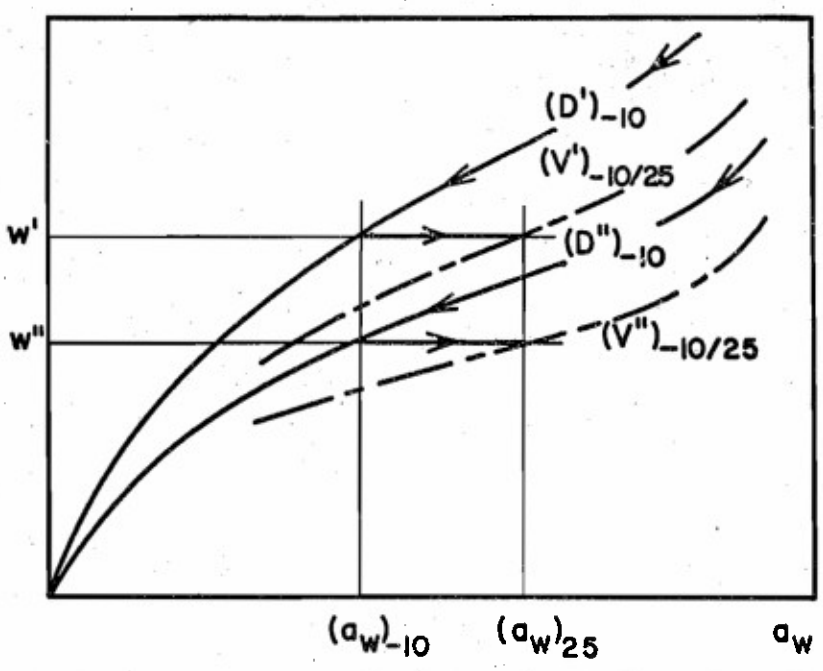


FIGURE 35. Hypothetical situation encountered where two materials,(') and ("), are subjected together to limited freeze-drying. Water does not redistribute on rewarming.

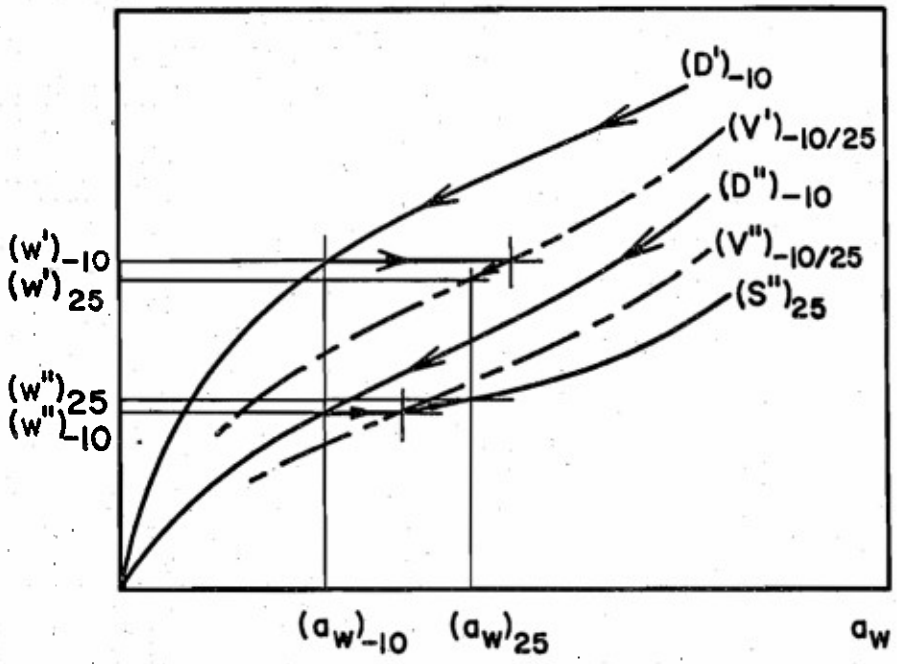
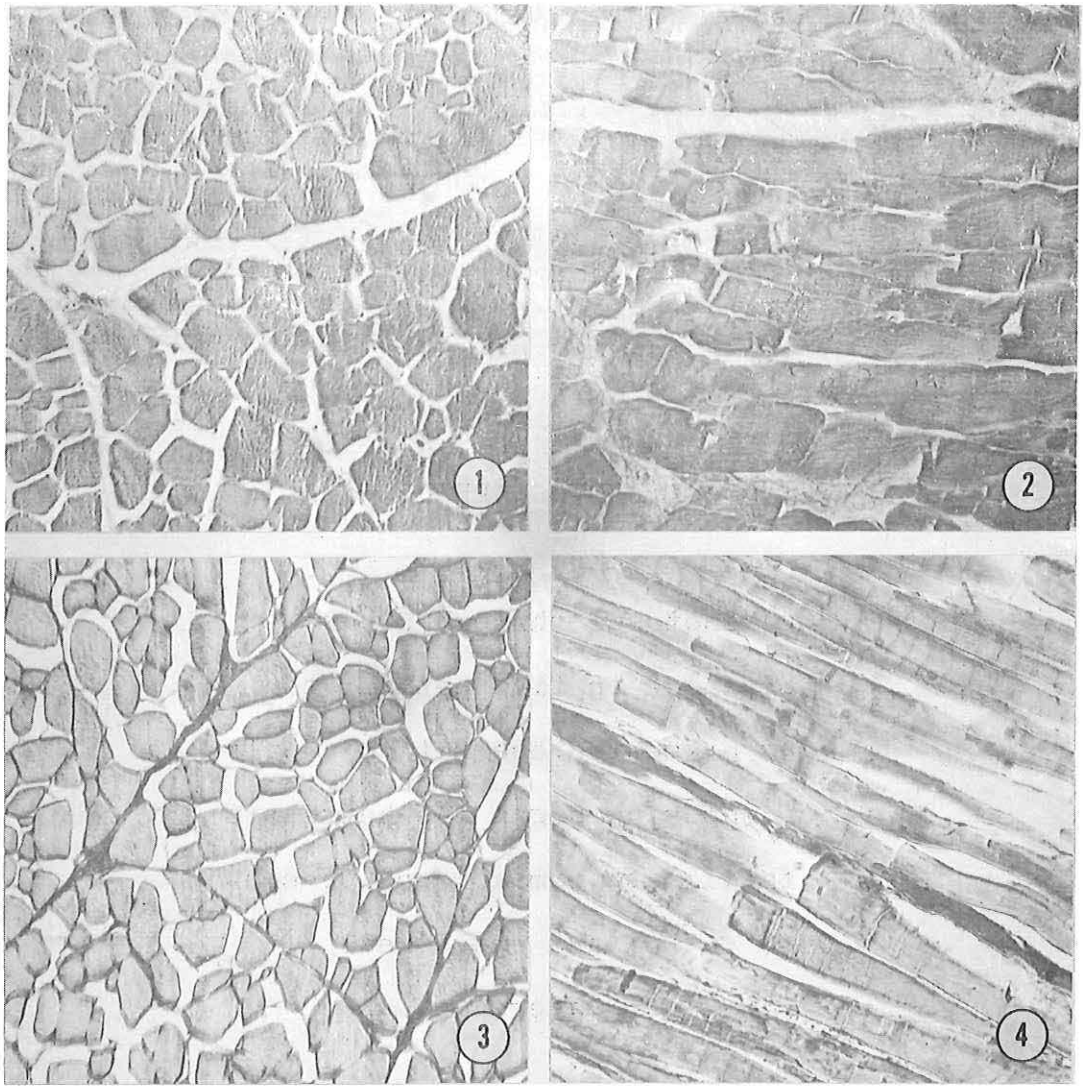


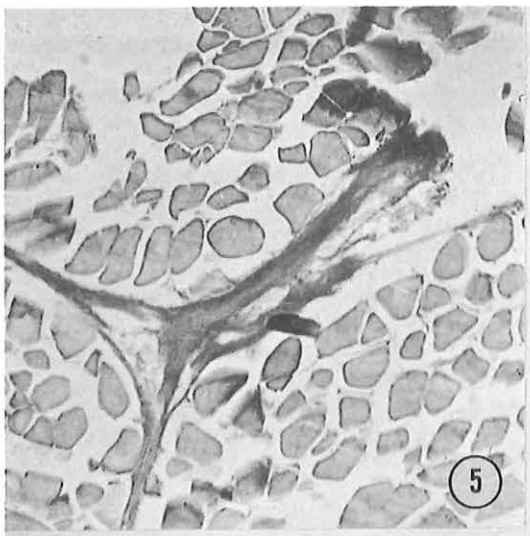
FIGURE 36. Hypothetical situation encountered where two materials, (') and ("), are subjected together to limited freeze-drying. Water redistributes on rewarming.

PHOTOGRAPHS

Photos 1 through 50 are arranged in five sets of ten and presented one set to a pair of opposing pages the better to facilitate comparisons of control and processed materials.



Photos 1 through 10: beef, cooked.
Photos 1 & 2: control preparations, fixed, etc.
Photos 3 & 4: control preparations, slowly frozen, freeze-dried, rehydrated, fixed, etc.
Photos 5 & 6: slowly frozen, freeze-dried, equilibrated to 0.20 a_w, compressed (500 p.s.i.), rehydrated, fixed, etc.
Photos 7 & 8: slowly frozen, freeze-dried, equilibrated to 0.50 a_w, compressed (500 p.s.i.), rehydrated, fixed, etc.
Photos 9 & 10: slowly frozen, freeze-dried, equilibrated to 0.80 a_w, compressed (500 p.s.i.), rehydrated, fixed, etc.
Photos 1, 3, 5, 7, 9: cross sections. Photos 2, 4, 6, 8, 10: longitudinal sections. Section thicknesses: Photos 1, 3, 5, 7, 8, 10: 10μ; Photos 2, 4, 6, 9: 15μ. Magnification: ×100.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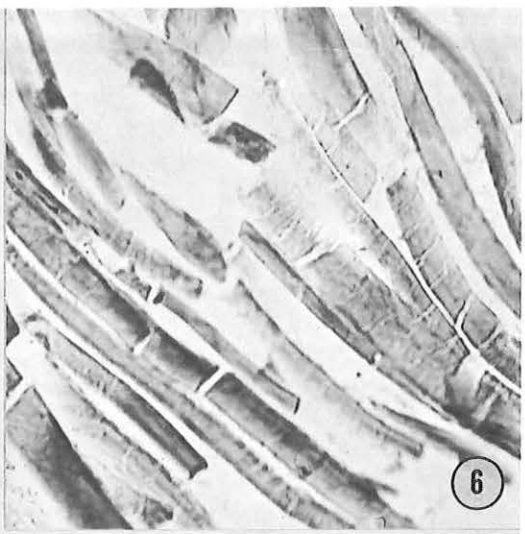
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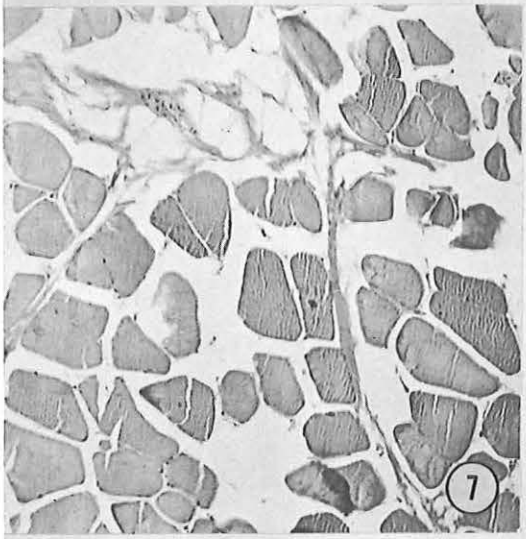
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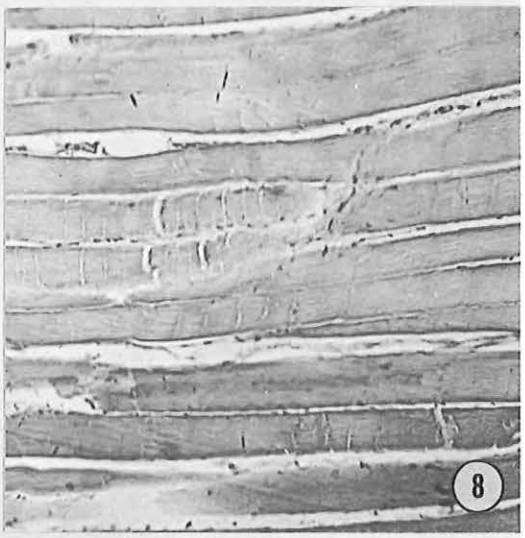
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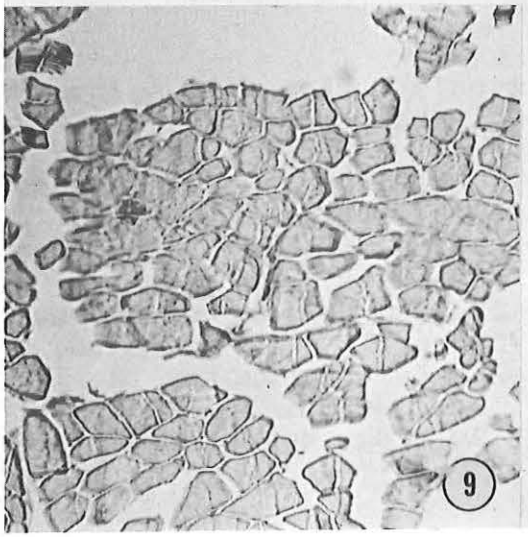
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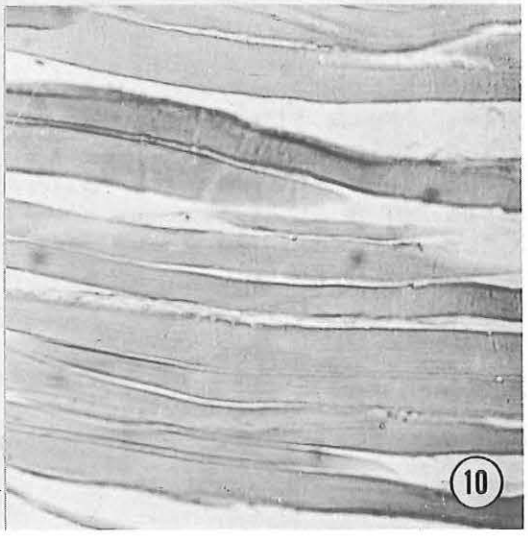
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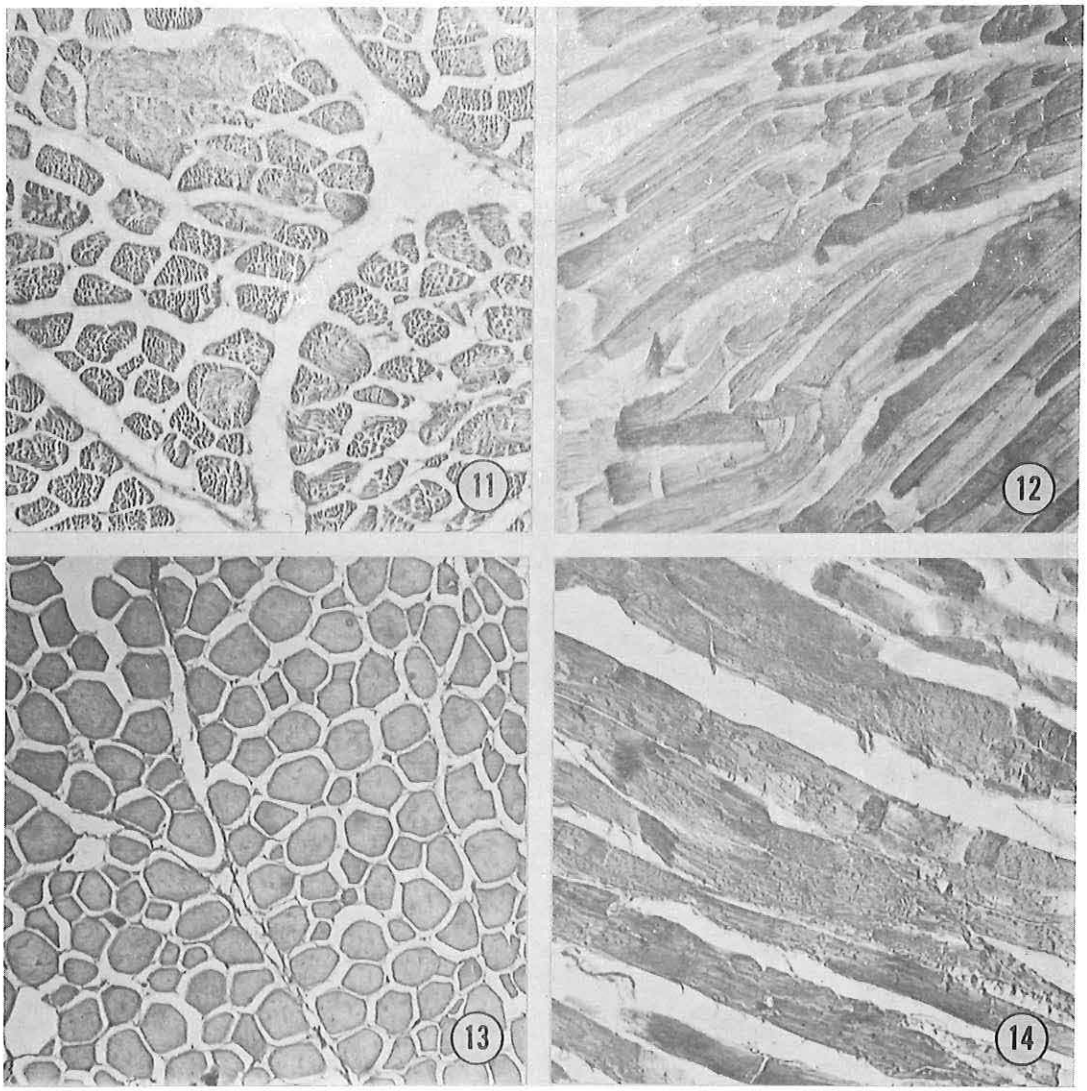
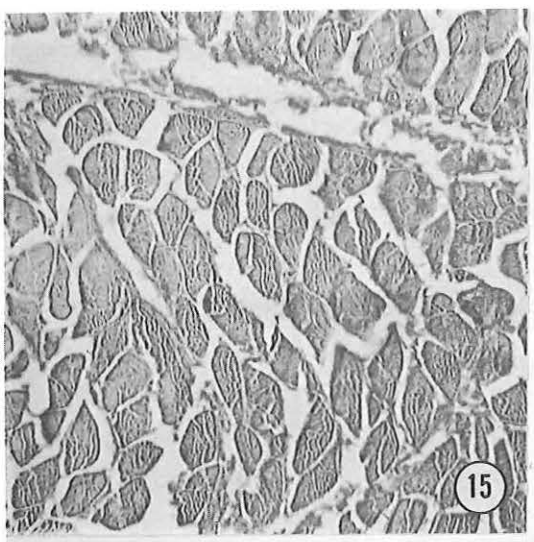


Photos 11 through 20: chicken muscle. Photos 11 & 12: controls, fresh tissue, fixed, etc. Photos 13 & 14: controls, cooked, slowly frozen, freeze-dried, rehydrated, fixed, etc. Photos 15 & 16: cooked, slowly frozen, freeze-dried, equilibrated to 0.40 a_w, compressed (500 p.s.i.), rehydrated, etc. Photos 17 & 18: cooked, slowly frozen, freeze-dried, equilibrated to 0.60 a_w, compressed (500 p.s.i.), rehydrated, etc. Photos 19 & 20: cooked, slowly frozen, freeze-dried, equilibrated to 0.80 a_w, compressed (500 p.s.i.), rehydrated, etc. Photos 11, 13, 15, 17, 19: cross sections. Photos 12, 14, 16, 18, 20: longitudinal sections. Section thicknesses: Photos 11 & 12: 15μ; Photos 13 through 20: 10μ. Magnification: ×100.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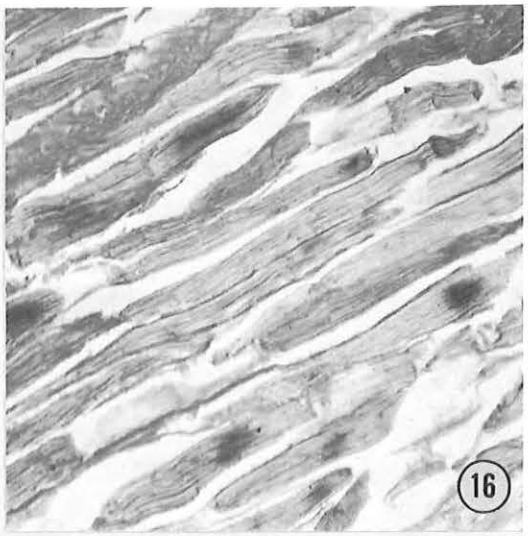
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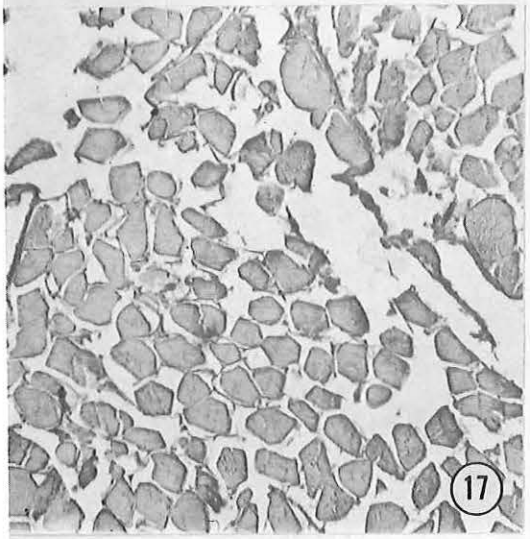
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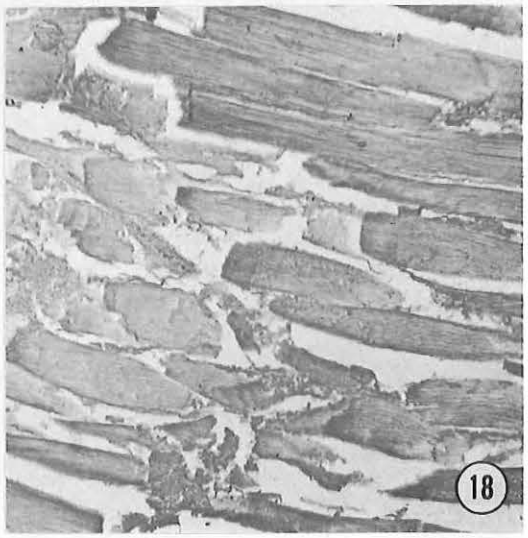
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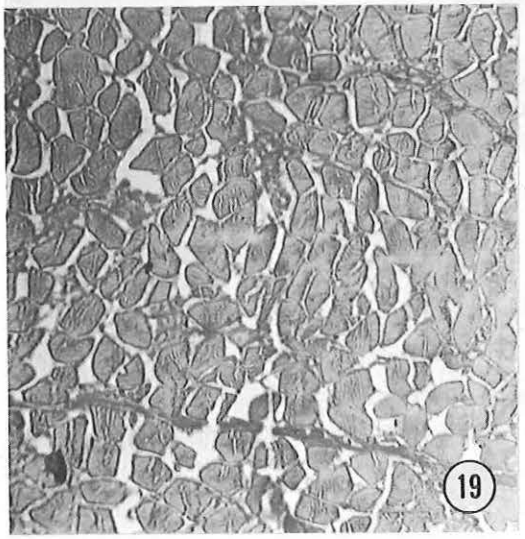
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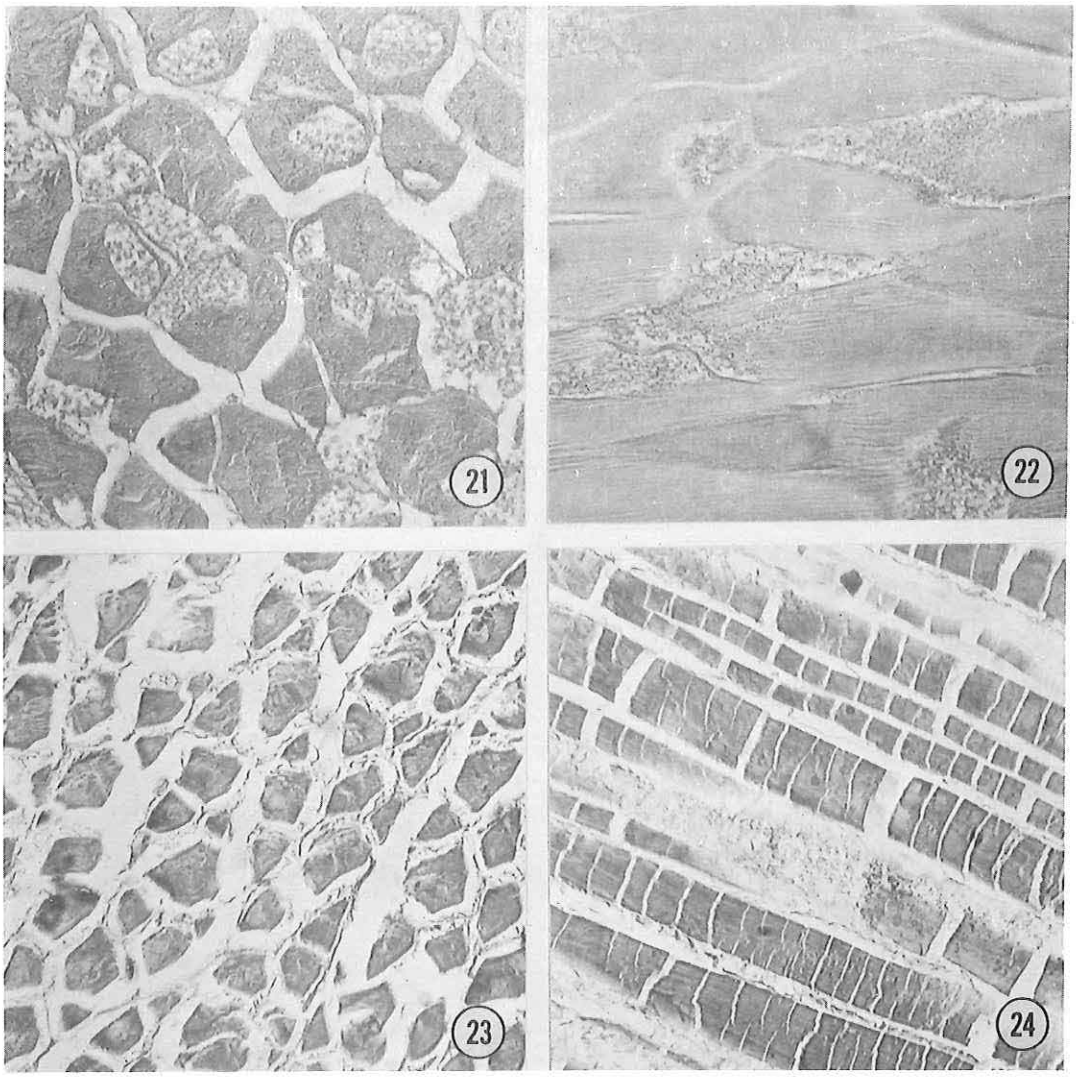
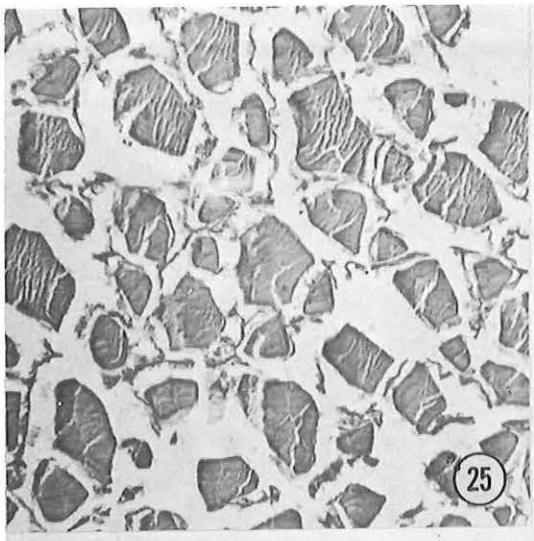


Photos 21 through 30: tuna, canned, water-pack.
Photos 21 & 22: control preparations, fixed, etc.
Photos 23 & 24: control preparations, slowly frozen, freeze-dried, rehydrated, fixed, etc.
Photos 25 & 26: slowly frozen, freeze-dried, equilibrated to 0.40 a_w, compressed (500 p.s.i.), rehydrated, fixed, etc.
Photos 27 & 28: slowly frozen, freeze-dried, equilibrated to 0.60 a_w, compressed (500 p.s.i.), rehydrated, fixed, etc.
Photos 29 & 30: slowly frozen, freeze-dried, equilibrated to 0.80 a_w, compressed (500 p.s.i.), rehydrated, fixed, etc.
Photos 21, 23, 25, 27, 29: cross sections. Photos 22, 24, 26, 28, 30: longitudinal sections. Section thicknesses: Photos 21 & 23 through 30: 10μ; Photo 22: 15μ. Magnification: ×100.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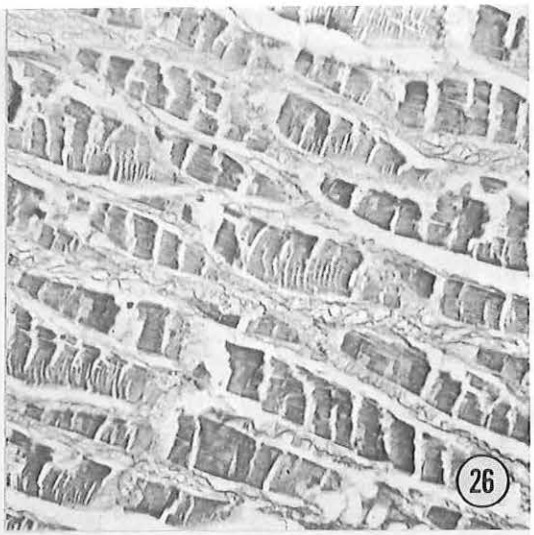
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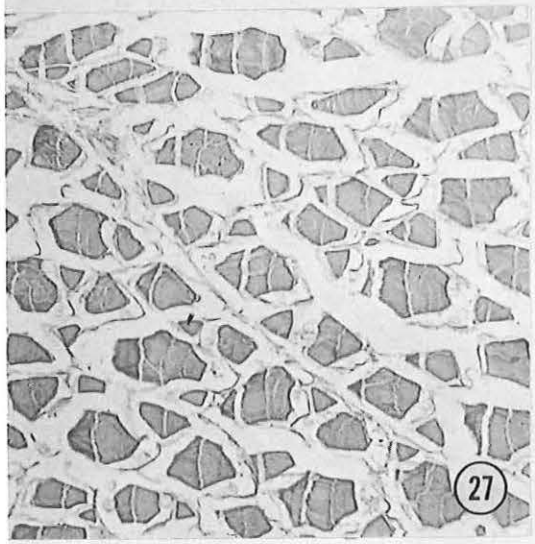
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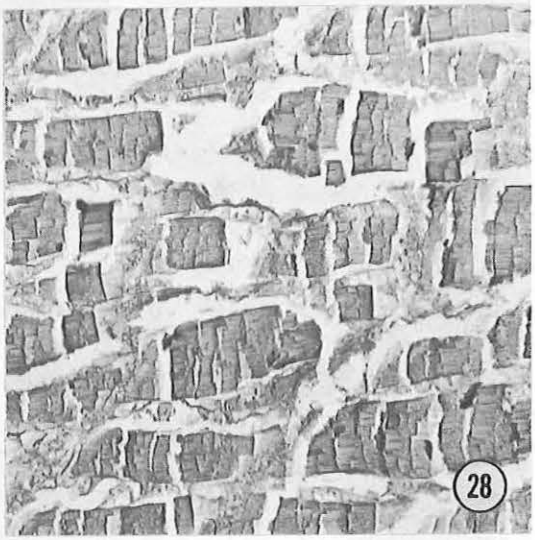
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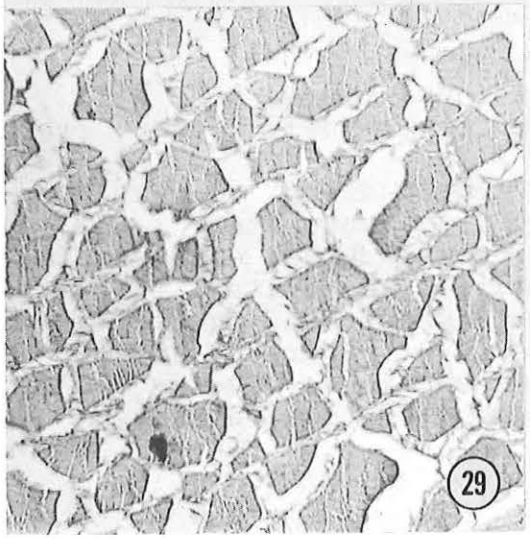
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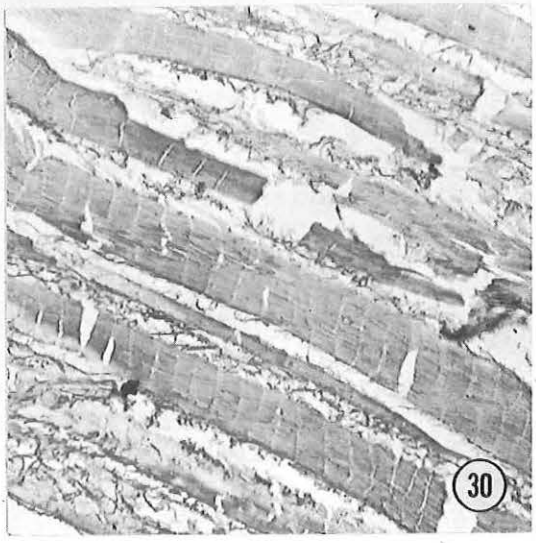
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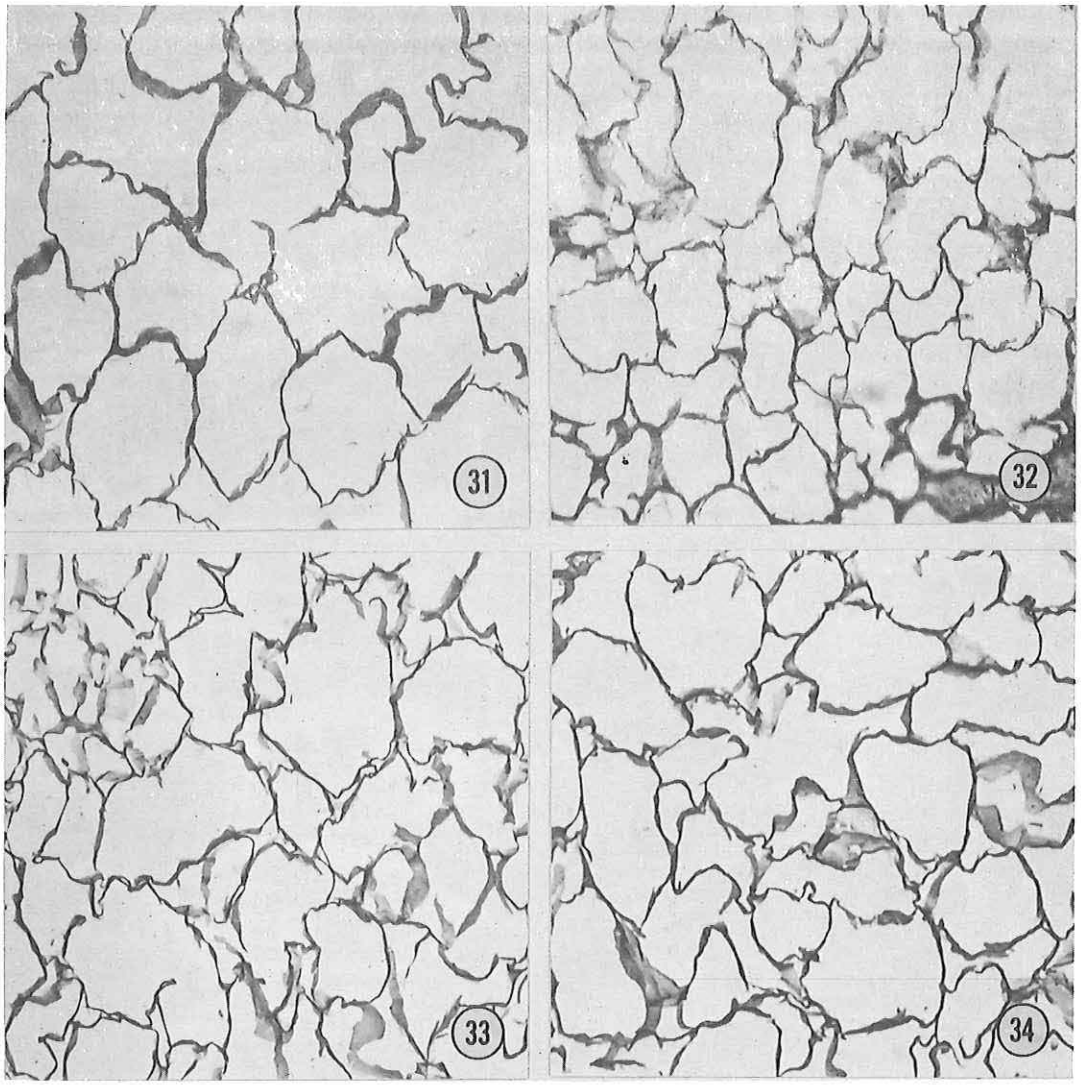
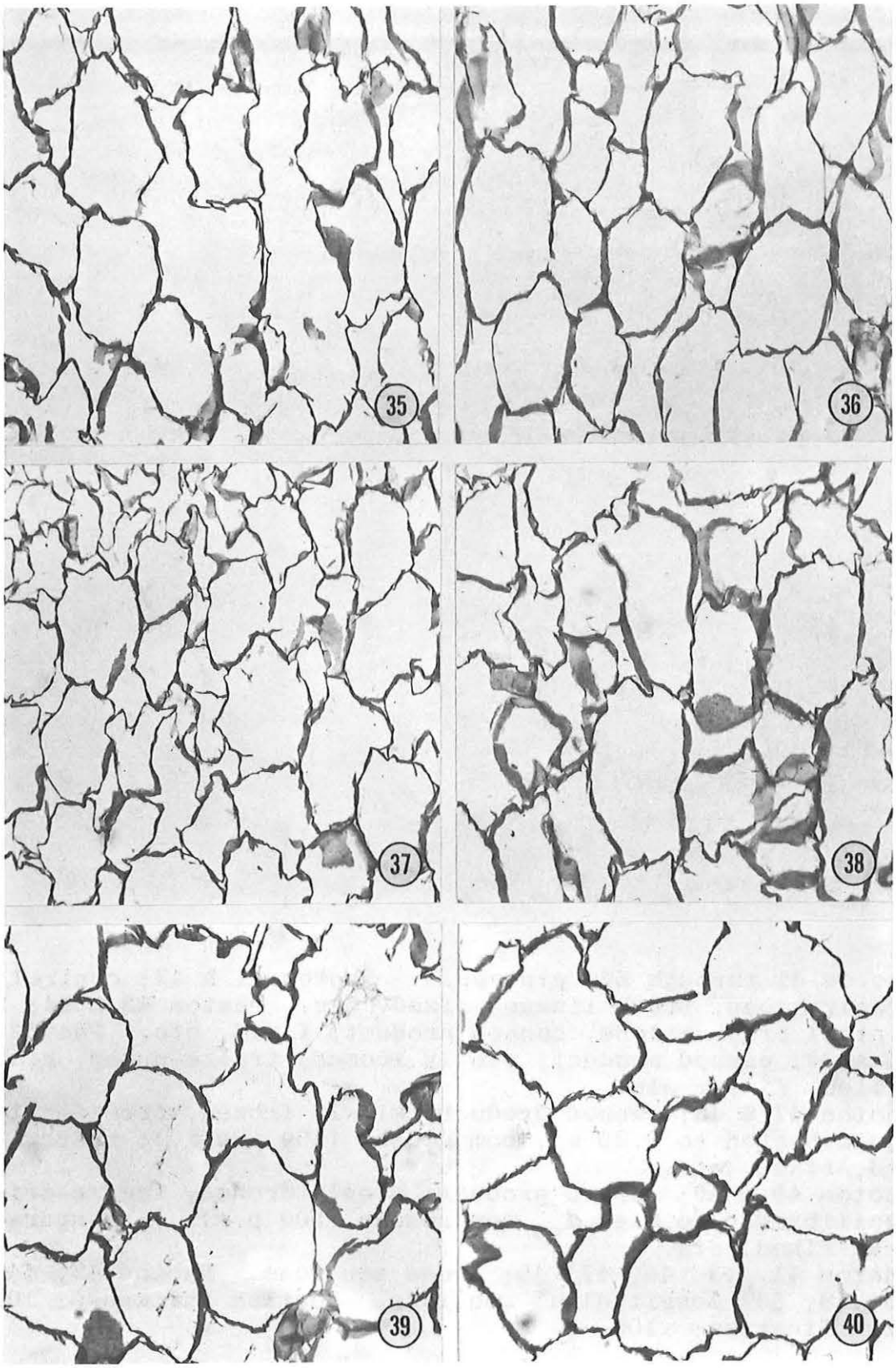


Photos 31 through 40: apple, fresh.
Photos 31 & 32: control preparations, fixed, etc.
Photos 33 & 34: control preparations, slowly frozen, freeze-dried, rehydrated, fixed, etc.
Photos 35 & 36: slowly frozen, freeze-dried, equilibrated to 0.20 a_w, compressed (500 p.s.i.), rehydrated, fixed, etc.
Photos 37 & 38: slowly frozen, freeze-dried, equilibrated to 0.40 a_w, compressed (500 p.s.i.), rehydrated, fixed, etc.
Photos 39 & 40: slowly frozen, freeze-dried, equilibrated to 0.60 a_w, compressed (500 p.s.i.), rehydrated, fixed, etc.
Photos 31, 33, 35, 37, 39: cross sections. Photos 32, 34, 36, 38, 40: longitudinal sections. Section thickness: 10μ.
Magnification: ×100.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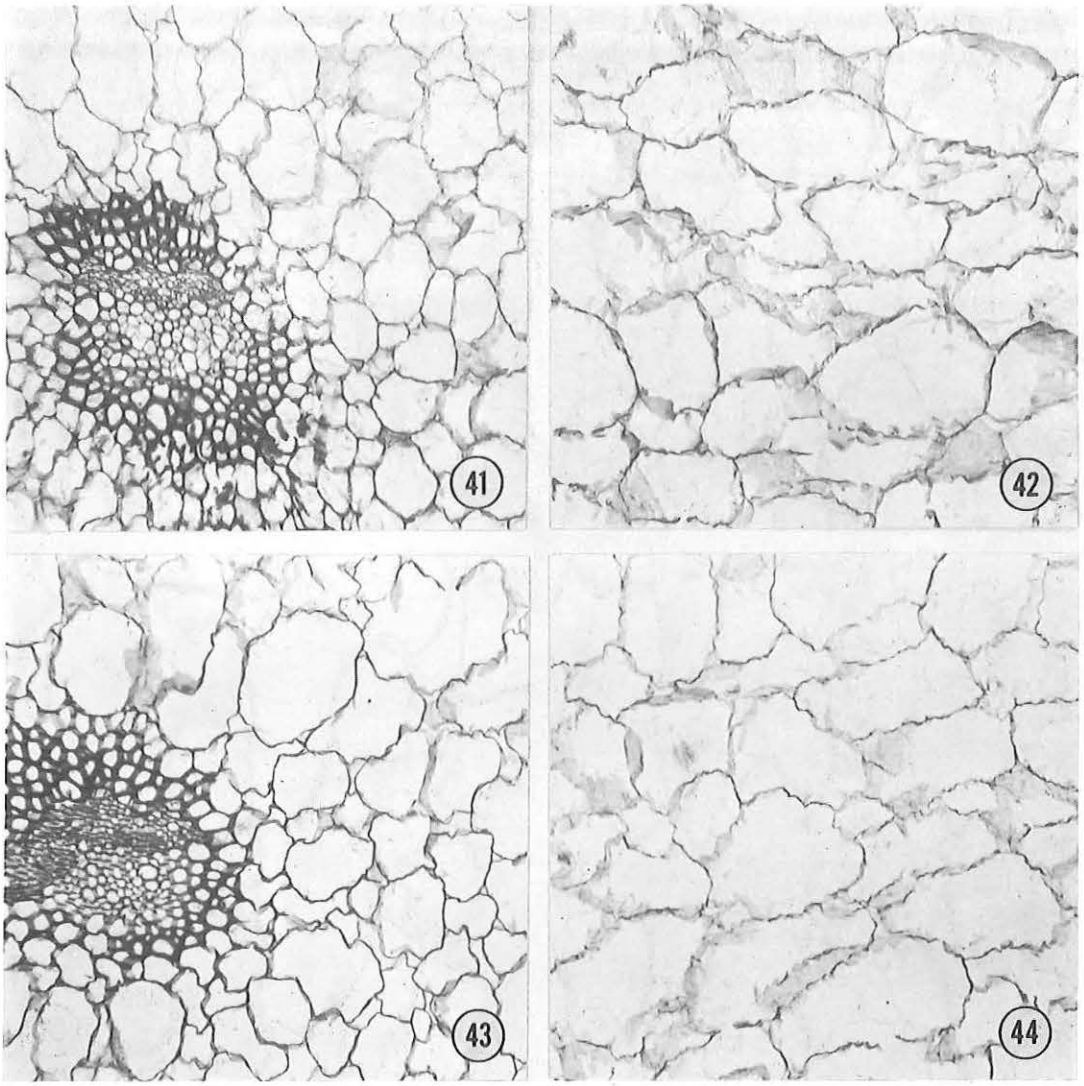
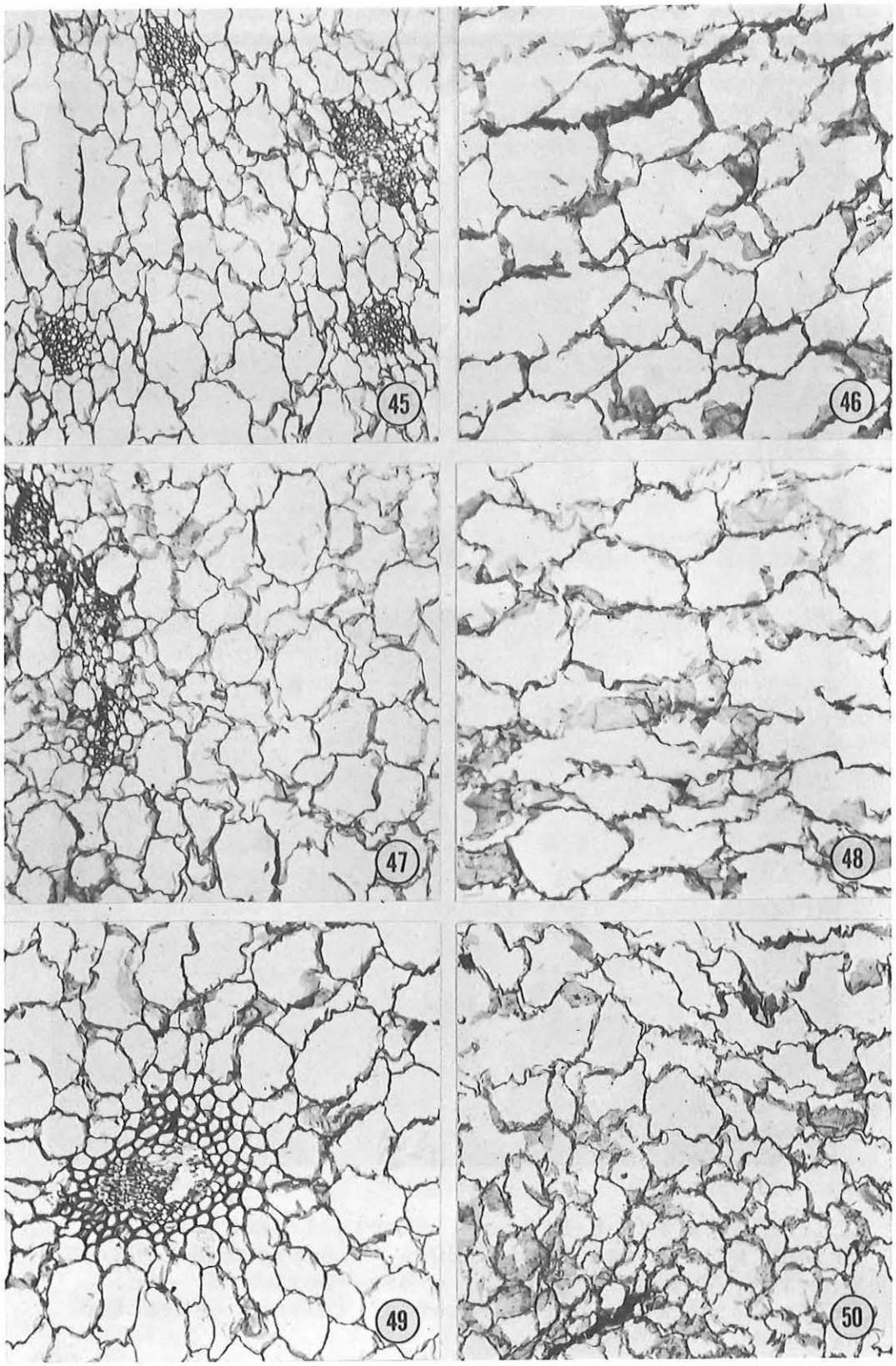


Photos 41 through 50: pineapple. Photos 41 & 42: control preparations, fresh tissue, fixed, etc. Photos 43 & 44: control preparations, canned product, fixed, etc. Photos 45 & 46: canned product, slowly frozen, freeze-dried, rehydrated, fixed, etc.
Photos 47 & 48: canned product, slowly frozen, freeze-dried, equilibrated to 0.25 a_w, compressed (500 p.s.i.), rehydrated, fixed, etc.
Photos 49 & 50: canned product, slowly frozen, freeze-dried, equilibrated to 0.40 a_w, compressed (500 p.s.i.), rehydrated, fixed, etc.
Photos 41, 43, 45, 47, 49: cross sections. Photos 42, 44, 46, 48, 50: longitudinal sections. Section thickness: 10μ. Magnification: ×100.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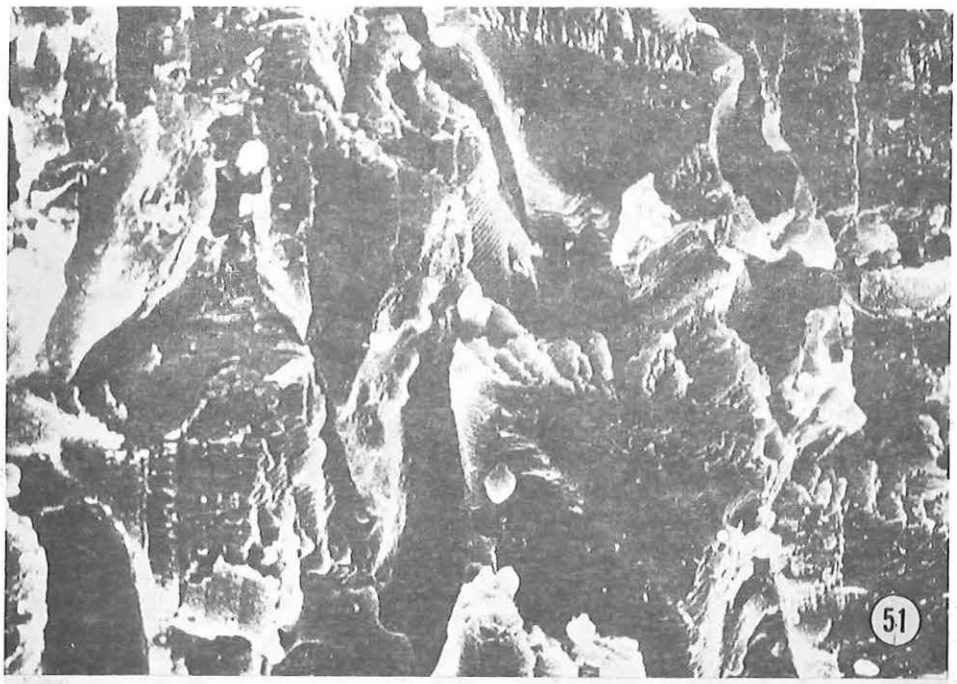
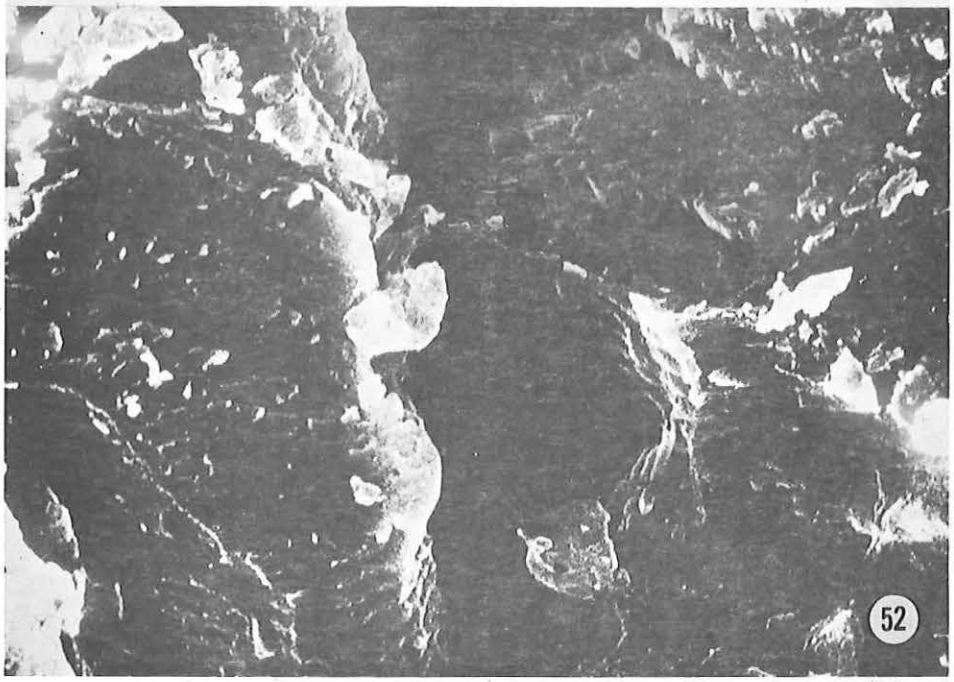
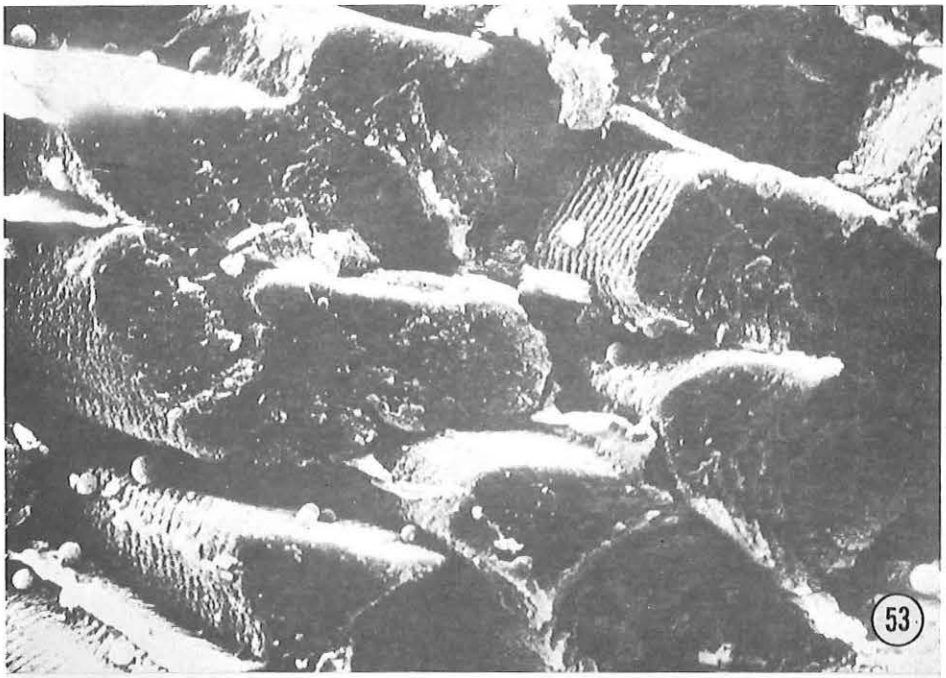
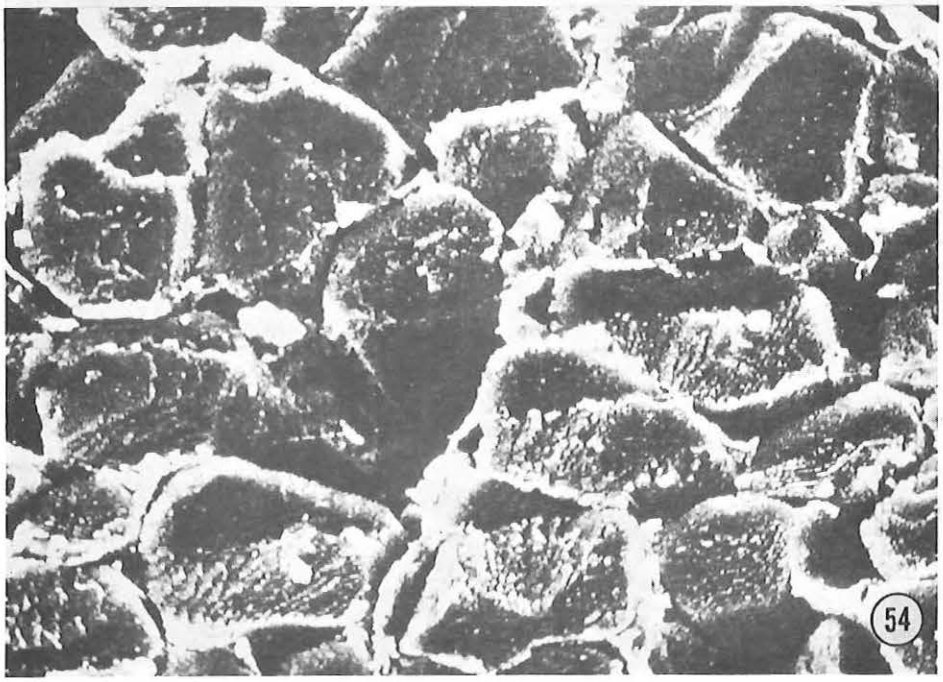


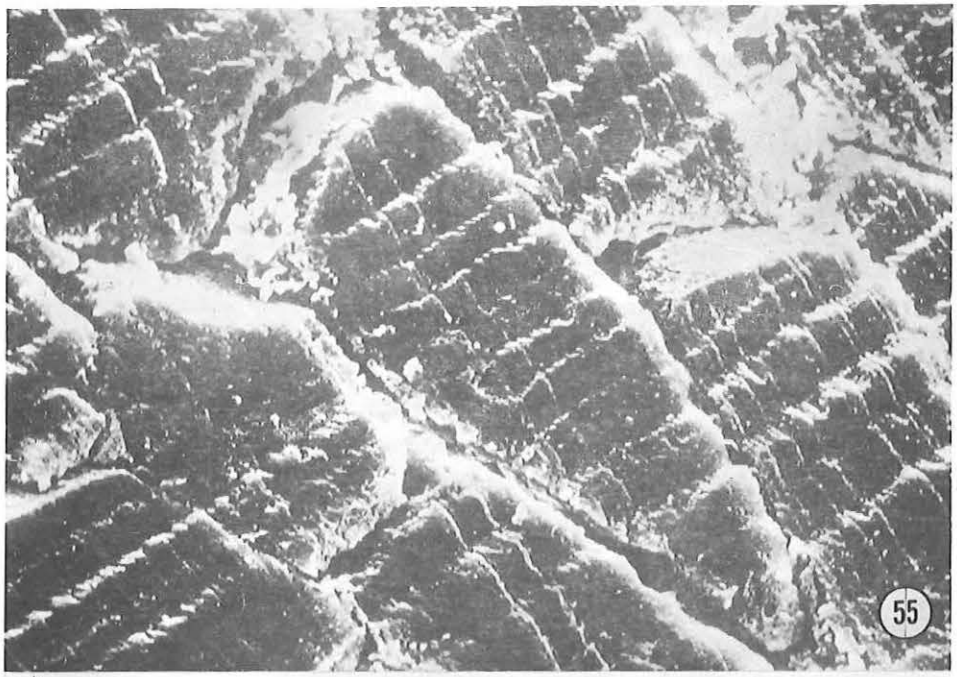


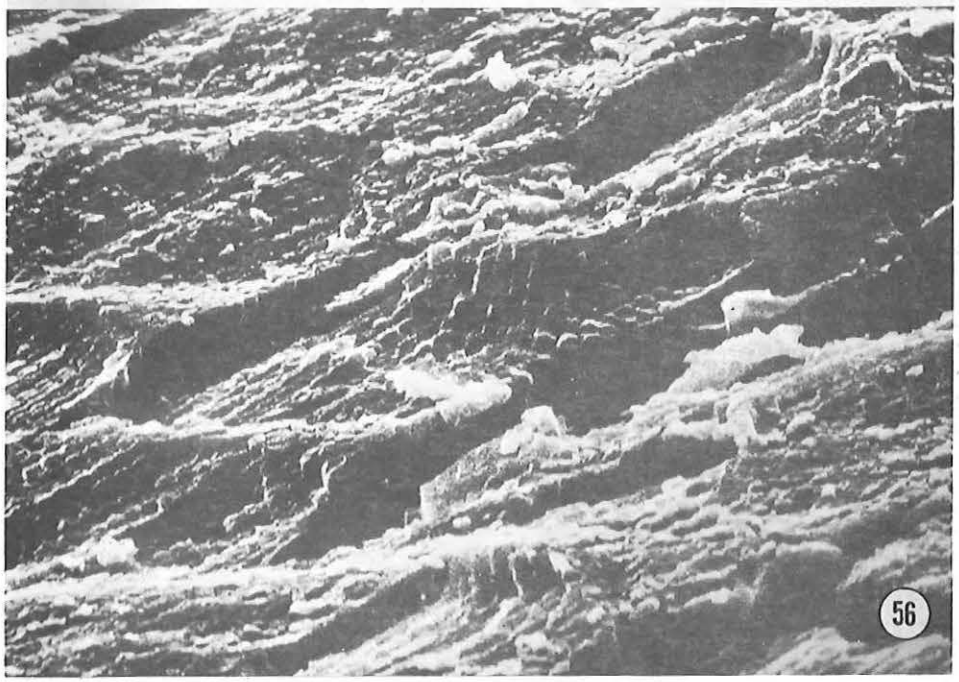
Photos 51 & 52: beef, raw, slowly frozen, freeze-dried, equilibrated to 0.20 a_w, compressed (500 p.s.i.), dried, embedded, cross-sectioned, etc.
Photo 51: freeze-dried material solvent extracted prior to moistening.
Scanning electron micrographs. Magnification: ×2,000.





Photos 53 & 54: beef, raw, slowly frozen, freeze-dried, equilibrated to 0.50 a_w, compressed (500 p.s.i.), dried, embedded, cross-sectioned, etc.
Photo 53: freeze-dried material solvent extracted prior to moistening.
Scanning electron micrographs. Magnifications: Photo 53: ×1,000; Photo 54: ×750.





Photos 55 & 56: beef, raw, slowly frozen, freeze-dried, equilibrated to 0.80 a_w, compressed (500 p.s.i.), dried, embedded, cross-sectioned, etc.
Photo 55: freeze-dried material solvent extracted prior to moistening.
Scanning electron micrographs. Magnifications: Photo 55: ×1,000; Photo 56: ×2,000.

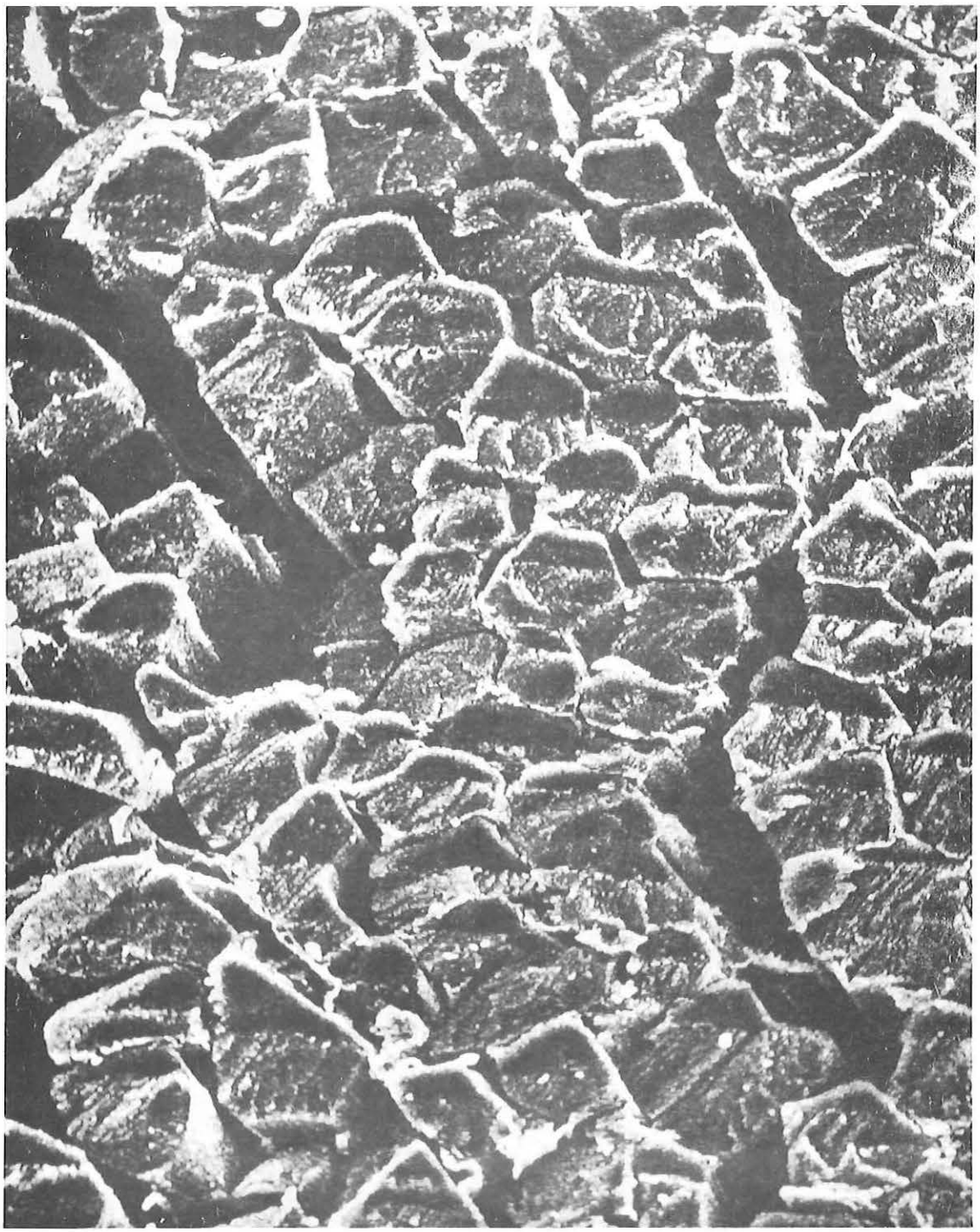


Photo 57: beef, raw, slowly frozen, freeze-dried, equilibrated to 0.50 a_w, compressed (500 p.s.i.), dried, embedded, cross-sectioned, etc. Scanning electron micrograph. ×500.

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APPENDIX

Standard values for vapor pressures of water and ice and working data derived from the former are presented for reference purposes the better to permit, for example, the duplication of procedures of the type described in the foregoing report.

TABLE XIII. TEMPERATURE DEPENDENCE OF THE VAPOR PRESSURES OF WATER AND ICE AND THE RATIO OF THE LATTER TO THE FORMER

temperature (°C.)	p_{water} (mm. Hg)	p_{ice} (mm. Hg)	p_{ice} * p_{water}
0	4.5808	4.580	1.0000
-1	4.2585	4.217	.9902
-2	3.9565	3.880	.9806
-3	3.6736	3.568	.9712
-4	3.4088	3.279	.9619
-5	3.1611	3.011	.9525
-6	2.9296	2.764	.9434
-7	2.7133	2.534	.9339
-8	2.5113	2.323	.9250
-9	2.3228	2.128	.9160
-10	2.1470	1.948	.9072
-11	1.9832	1.782	.8985
-12	1.8307	1.629	.8898
-13	1.6886	1.488	.8812
-14	1.5566	1.358	.8724
-15	1.4339	1.239	.8640
-16	1.3198	1.1295	.8558
-17	1.2140	1.0283	.8470
-18	1.1158	.9360	.8388
-19	1.0248	.8513	.8306
-20	.9405	.7740	.8229
-21	.8625	.7028	.8148
-22	.7904	.6377	.8068
-23	.7237	.5782	.7989
-24	.6620	.5239	.7913

(continued)

TABLE XIII (continued)

temperature (°C.)	p_{water} (mm. Hg)	p_{ice} (mm. Hg)	p_{ice} / p_{water} *
-25	0.6053	.4742	.7834
-26	0.5528	.4290	.7760
-27	0.5045	.3878	.7686
-28	0.4600	.3502	.7613
-29	0.4192	.3160	.7538
-30	0.3816	.2849	.7465
-31	0.3471	.2566	.7392
-32	0.3154	.2309	.7320
-33	0.2864	.2077	.7252
-34	0.2597	.1866	.7185
-35	0.2354	.1675	.7115
-36	0.2132	.1502	.7045
-37	0.1928	.1346	.6981
-38	0.1742	.1205	.6917
-39	0.1573	.1077	.6846
-40	0.1418	.0962	.6784
-41	0.1278	.0859	.6721
-42	0.1151	.0766	.6655
-43	0.1034	.0683	.6605
-44	0.0929	.0608	.6544
-45	0.0833	.0540	.6482
-46	0.0747	.0479	.6412
-47	0.0669	.0425	.6352
-48	0.0585	.0377	.6444
-49	0.0534	.0334	.6254
-50	0.0477	.0296	.6205

* This ratio is, by definition, the water activity of the ice.

TABLE XIV. CONDENSER TEMPERATURES PROVIDING DESIRED WATER ACTIVITIES AT SELECTED SAMPLE TEMPERATURES

	Sample Temperatures (°C.)				
a_w	-10	-20	-30	-40	-50
1.00	-8.90	-17.96	-27.16	-36.50	-46.0
.90	-10.10	-19.06	-28.20	-37.50	-46.9
.80	-11.42	-20.30	-29.34	-38.54	-47.9
.70	-12.89	-21.68	-30.63	-39.73	-49.0
.60	-14.59	-23.26	-32.08	-41.09	-50.3
.50	-16.55	-25.09	-33.80	-42.69	-51.5
.40	-18.91	-27.31	-35.86	-44.60	-53.4
.30	-21.91	-30.10	-38.47	-47.00	-55.7
.20	-25.99	-33.93	-42.04	-50.4	-59.4
.15	-28.82	-36.58	-44.53	-52.7	-61.0
.10	-32.70	-40.20	-47.90	-55.8	-64.0
.05	-39.03	-46.17	-53.0	-61.0	-68.7
.025	-45.0	-51.0	-58.8	-65.9	-73.0

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13. ABSTRACT

Twelve foods, alone and in combination, were frozen at various rates, freeze-dried in different ways and brought to certain predetermined water contents by exposure, via the vapor phase, to water at controlled activities (a_w's). The moist freeze-dried materials were subjected to compression and to further drying, after which they were rehydrated.

It was found that processing conditions insuring best recoveries could be defined in terms of water activities to which foods were adjusted prior to compression; that is, the conclusion drawn on the basis of the Phase I studies was confirmed and extended. It was, moreover, shown that composite foods were more likely to respond well to compression where component items were selected on the basis of compatible a_w-dependent behavior.

The times taken by foods freeze-dried by conventional methods to reach constant water contents by contact with atmospheres of intermediate a_w were found not to exceed several hours. Moistening via the vapor phase proved to possess special advantages where foods destined for compression were freeze-dried in admixture.

Freeze-drying by sublimation and direct desorption of remaining water to various predetermined water activities was subjected to further analysis. Pilot-scale apparatus was designed, constructed, tested, and operated successfully.

Supplementary studies were completed in continued attempts to define factors responsible for recovery. Whole and solvent-extracted foods were examined by light and scanning electron microscopic techniques. Indications of the nature of certain irreversible changes resulting from compression were obtained.

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	ROLE	WT	ROLE	WT	ROLE	WT
Recovery	8,7		4			
Rehydration	8,7		4			
Freeze dried foods	9,7		9			
Compressed foods	9,7		9			
Humidity	6					
Moisture content	6					
Vacuum	6					
Water activity	6					
Examination			8			
Electron microscopes			10			
Light (visible radiation)			10			
Changes			9			